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RADIATIVE EFFECTS ON EXPLOSIVE INSTABILITY

FINAL REPORT

CONTRACT AF 04(611)-10928

January 1967

**A. L. Berlad
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FOREWORD

Defense Research Corporation has assigned a secondary report number, CR-10928-4, to identify the report prior to approval and as an internal control

THIS TECHNICAL REPORT HAS BEEN REVIEWED AND IS APPROVED.

**W. H. EBELKE, Colonel, USAF
Chief, Propellant Division**

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ABSTRACT

The explosion limits associated with a given sample of an unstable compound are generally taken to be defined by the sample's temperature, pressure, composition, and size. In the presence of steady-state or pulsed radiative fields, these explosion limits are necessarily modified. Further, photochemically significant radiation (e.g., U.V.) may play a markedly different role in this modification than does purely thermal radiation (I.R.). Examination is made of the role of both steady-state and pulsed radiative fields in the explosive behavior of unstable compounds. The analytic considerations are illustrated for the case of the mixed hydrazine family of reactants as well as for ozone.

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NOMENCLATURE

- A = a reactive intermediate in the decomposition of N_2H_4 and related compounds (see Appendix I), moles/cm³
- A_1 = O-atom concentration, moles/cm³
- A_e = concentration of [1D] atomic oxygen, moles/cm³
- B = a reactive intermediate in the decomposition of N_2H_4 and related compounds (see Appendix I), moles/cm³
- B_e = concentration of [$^3\Sigma_u^-$] diatomic oxygen, moles/cm³
- B_S = concentration of a reactive intermediate in the ordinary quasi-steady state, moles/cm³
- B_{PS} = concentration of a reactive intermediate in the photochemical quasi-steady state, moles/cm³
- c_p = heat capacity, cal/gm/°K
- d = characteristic dimension (cylinder diameter) for the sample of unstable compound, cm
- D_A = diffusion coefficient for species A and the remainder of the gas, cm²/s
- D_B = diffusion coefficient for species B and the remainder of the gas, cm²/s
- E_D = dissociation energy, calories/mole
- E_e = energy of electronically excited oxygen atoms, calories/mole
- E_v = energy per mole of photochemically significant photons, calories/mole
- F = reactant concentration, moles/cm³

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- F_0 = initial value of reactant concentration, moles/cm³
- \bar{J}_{th} = volumetric radiative energy source function, calories/cm³/s
- h = Planck's constant
- h_i = heat of reaction for the i th kinetic step, where $i = 1, 2$, etc., calories/mole
- k_i = rate constant for the i th kinetic step, where $i = 1, 2$, etc.
- k_v = rate constant for the photodissociative step, s⁻¹
- \dot{q} = heat loss rate, cal/cm³/s
- \mathcal{L}_c = volumetric (average) conduction heat loss rate, calories/cm³/s
- \mathcal{L}_r = volumetric radiative energy loss rate, calories/cm³/s
- M = third body concentration, moles/cm³
- n = number of moles of reactant decomposed per unit volume by a short radiative pulse, moles/cm³
- $[O]$ = concentration of ground-state atomic oxygen, moles/cm³
- $[O^*]$ = concentration of electronically excited atomic oxygen, [¹D], moles/cm³
- $[O_2^*]$ = concentration of electronically excited diatomic oxygen [³Σ_u⁻], moles/cm³
- P = a product molecule, moles/cm³
- \dot{q}''' = heat release rate, calories/cm³/s
- R_i = reaction rate for the i th kinetic step, where $i = 1, 2$, etc., moles/cm³/s
- R_v = reaction rate for the photodissociative kinetic step, moles/cm³/s
- T = temperature, °K
- t = time, s
- T_1 = stable steady-state temperature for the unstable medium, °K

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- T_2 = unstable steady-state temperature for the unstable medium, $^{\circ}\text{K}$
- T_{12} = critical temperature for explosion of the unstable medium, $^{\circ}\text{K}$
- T_b = environment (bath) temperature for the unstable medium, $^{\circ}\text{K}$
- T_{bc} = critical bath temperature for explosion, $^{\circ}\text{K}$
- T_s = temperature of the quasi-steady sample of an unstable compound, $^{\circ}\text{K}$
- T_{ps} = temperature of the sample of an unstable compound under photo-chemical quasi-steady state conditions, $^{\circ}\text{K}$
- ΔB = instantaneous concentration rise due to an arbitrarily short radiative pulse, moles/cm³
- ΔT = instantaneous temperature rise due to an arbitrarily short radiative pulse, $^{\circ}\text{K}$
- λ = thermal conductivity, calories/cm/s/ $^{\circ}\text{K}$
- ν = frequency, s⁻¹
- ρ = density, gm/cm³
- MMH = Monomethylhydrazine
- UDMH = unsymmetrical dimethylhydrazine

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I. INTRODUCTION

An unstable compound in a given apparatus is characterized by pressure-temperature-composition regimes which correspond to explosive or non-explosive conditions. These are the well known explosion limits. Implicit in this experimental definition of an explosion limit is the absence of an external radiative field which could influence either the thermal or the chemical properties of the potentially explosive system. Where such a radiative field exists, its effects on the explosive properties of the unstable compound must be considered. Such consideration is of more than pure academic interest. For example, rocket engine environments generally contain strong sources of radiation which can induce both thermal and photochemical effects in an unreacted unstable compound; such as: hydrazine, any member of the mixed hydrazine family of reactants, ozone, ozone-halogen reactants, and many others. The rocket engine radiative environment experienced by a sample of an injected unstable compound corresponds to an intense radiative transient. Properties of this radiation field (together with the other engine environmental features) are required to prescribe the explosion conditions for the unstable compound.

Another case of interest is that associated with the well known flash photolysis experiments. Here again, a transient radiative field, containing both thermally and photochemically significant radiation, plays a role in the explosion phenomenon. Another case of practical interest is exemplified by a given sample of an unstable compound subjected to a far less intense but steady radiative field. Such a sample has its normal explosion limits affected by the radiative field.

It is the purpose of this study to examine the various ways in which photochemically and thermally significant radiation, both transient and steady, can affect explosion limits of unstable materials.

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II. RADIATIVE EFFECTS ON EXPLOSIONS

Both energy and mass conservation equations may be utilized to prescribe explosive instability features which are unobtainable¹ or less fully prescribed by classical consideration^{2,3} of only one equation or the other.

For ultraviolet absorption by an unstable sample (such as ozone or hydrazine), the primary photochemical act involves creation of a predissociated state, followed by decomposition of the absorbing molecule and partial thermalization of the absorbed photon's energy. The thermalized portion of this energy source must be accounted for in the energy conservation equation. The remainder of the energy is used to generate dissociated molecular fragments, and corresponds to a kinetic source term that must be included in the mass conservation (kinetic) equations. Thus, the energy equation is written:

$$\dot{q}''' = \rho c_p \frac{\partial T}{\partial t} = \lambda V^2 T + \sum R_i h_i - \sum \dot{Q}_i + \dot{Q}_{th} \quad (1)$$

Additionally, the kinetic rate equations are coupled to equation (1). This coupling is illustrated below with the simplified kinetics as often considered⁴ for 100% ozone or hydrazine decomposition:



where the rates of the individual steps are given by the equations

$$R_v = k_v [F] \quad (5)$$

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$$R_1 = k_1[M][F] \quad (6)$$

$$R_2 = k_2[F][B] \quad (7)$$

etc.,

and where rates for the individual species take the form:

$$\frac{\partial[F]}{\partial t} = D_A \nabla^2 F - R_v - R_1 - R_2 \pm \dots \quad (8)$$

$$\frac{\partial[B]}{\partial t} = D_B \nabla^2 B + R_v + R_1 - R_2 \pm \dots \quad (9)$$

etc.

When the approximation of spatial homogeneity is permitted, equations (1), (8), and (9) become:

$$\rho c_p \frac{dT}{dt} = \sum R_i h_i - \mathcal{L}_r - \mathcal{L}_c + \mathcal{F}_{th} \quad (10)$$

and:

$$\frac{d[F]}{dt} = -R_v - R_1 - R_2 \quad (11)$$

$$\frac{d[B]}{dt} = R_v + R_1 - R_2 \quad (12)$$

etc., where all values are spatially averaged.

Under some circumstances, the explosion limits of such a system may be studied by the method of the phase plane, or by modified classical methods. Where characterization of the chemical kinetic scheme is more complex, or transient radiative fluxes are to be considered, direct

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integration of the coupled conservation equations may be necessary. The analytic approach to be taken differs with the nature and complexity of the specific case under consideration.

It is necessary to reemphasize the fact that the presence of an ultraviolet radiative field generally implies thermal as well as photochemical sources in the unstable medium. The relative significance of each type of source depends on many factors, particularly the chemical nature of the irradiated reactant. In general, however, analysis of photolysis requires that thermal, photokinetic, and the usual chemical kinetic effects all be considered.

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III. SPECIAL CASES INVOLVING RADIATIVE EFFECTS ON EXPLOSIONS

It is expected that analysis of the explosive behavior of a photochemically active unstable system will depend upon such features as the optical opacity of the medium as well as on the spectral and temporal structure of the incident radiative flux density. We here delineate several limiting cases and indicate the kinds of analyses that may be utilized in examining each case.

For the purposes of this discussion, we assume the sample is in a bath of temperature T_b and that, in the absence of radiation, explosion does not occur.

CASE (A): The optically thin sample is subjected to an arbitrarily short, intense u.v. pulse.

This case may be analyzed by the method of the phase plane. If E_v is the energy of an absorbed photon and $(E_v - E_D)$ the thermalized portion of this energy, then, the instantaneous initial temperature rise of the system is given by:

$$\Delta T = \frac{(E_v - E_D)n}{\rho c_p}, \quad (^\circ K). \quad (13)$$

For a reaction of the form



where B is some reactive molecular fragment produced by photodissociation of F, there is an "instantaneous" rise in the value of B, due to the flash:

$$\Delta B = 2n, \quad (\text{moles/cm}^3). \quad (15)$$

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In order to examine the stability of the flashed system one examines the new state coordinate $(T_1 + \Delta T, B_1 + \Delta B)$ on the phase plane, where (T_1, B_1) are the state coordinates prior to the flash. If $(T_1 + \Delta T, B_1 + \Delta B)$ falls on an unstable trajectory, explosion follows.

CASE (B): The optically thin sample is subjected to constant, steady-state u.v. flux.

This case may be analyzed by one of several methods. The steady-state u.v. flux changes the ordinary (quasi-steady) state to a photochemical steady state, or explosion occurs. Thus, if (T_S, B_S) are the space average values of T and B , prior to irradiation, they become T_{PS} and B_{PS} shortly after irradiation is started. Here $T_{PS} > T_S$ and $B_{PS} > B_S$. Either classical methods^{2,3} or the phase plane method¹ may be utilized (as appropriate) in the determination of the critical explosion conditions.

CASE (C): The optically thin sample is subjected to a nonsteady u.v. flux that ultimately becomes steady.

If the final steady state flux corresponds to an explosion condition (Case B), then explosion occurs. If the ultimately achieved steady state flux corresponds to a photochemical quasi-steady state, explosion may or may not occur prior to such time. In general, integration of the time-dependent equations [e.g., equations (10), (11), (12)] reveals whether explosion occurs or whether a photochemical quasi-steady state is achieved.

CASE (D): The optically thick sample is subjected to an arbitrarily short, intense u.v. pulse.

These initial conditions lead to inhomogeneous photoinitiation. The time and space integration of the more general conservation equations [e.g., equations (1), (8), and (9)] may be necessary to a determination of these effects.

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CASE (E): The optically thick sample is subjected to a steady-state u.v. flux.

These conditions lead to the establishment of a spatially non-homogeneous, photochemical quasi-steady state, or to nonhomogeneous photoinitiation. Explosion is taken to occur when there exists an upper limit on the u.v. radiative flux density which permits quasi-steady solutions to the nonhomogeneous conservation equations [e.g., equations (1), (8), (9)].

In the analyses appropriate to homogeneous explosion one requires knowledge of the chemical kinetics of the system involved. Additionally, the characterization of the photochemical steady state and the applicable time-dependent conservation equations are needed. For the mixed hydrazine family of fuels, these are considered in Appendix I.

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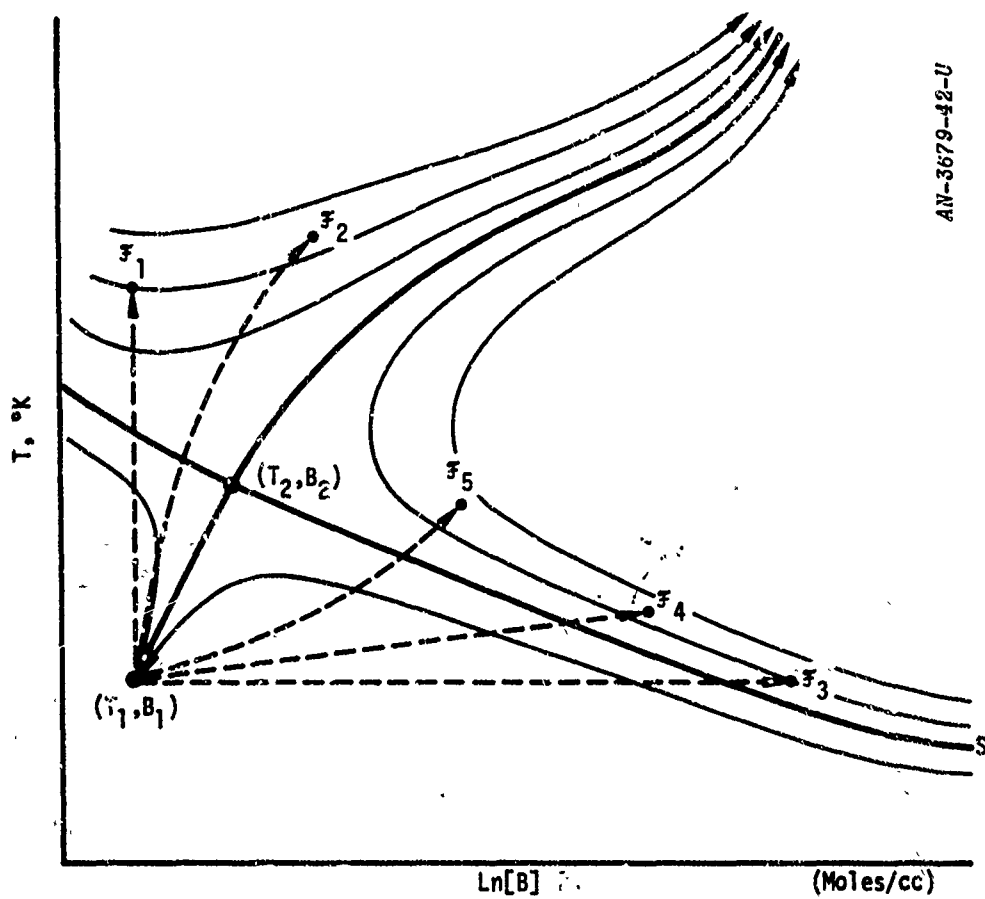
IV. EXPLOSIVE EFFECTS OF A RADIATIVE PULSE ON A QUASI-STEADY SAMPLE OF AN UNSTABLE COMPOUND

Based on these considerations, we now characterize the ways in which a thermally and/or photochemically significant radiative pulse can explosively modify the state of a quasi-steady sample of an unstable compound. An illustrative phase plane diagram is shown in Fig. 1. At time equals zero, and in the absence of radiation, the system is quasi-steady and the T-B values characterizing the system¹ are those of the stable nodal point, (T_1, B_1) . The unstable saddle point conditions are (T_2, B_2) . The separatrix, S, defines the boundaries between explosive and non-explosive trajectories. The explosive trajectories must, in a real case, approach a stable singularity associated with thermodynamic equilibrium.

In this phase plane diagram, we have indicated various ways (both real and hypothetical) in which the quasi-stable system can be radiatively exploded:

1. A thermal pulse, such as \mathcal{F}_1 , is represented by a straight vertical line. If the energy of the pulse is sufficient, the change in the originally stable system is characterized by a sharp temperature increase and the resultant unstable trajectory leads to explosion. Physically, such a case can only be approximated.
2. A thermal pulse, such as \mathcal{F}_2 , whose duration is comparable to the response time of the system, must be represented by a curved line. Although the primary act of photoabsorption does not result in dissociation of the unstable compound (and consequent production of [B]), the finite duration of the pulse requires that [B], as well as T, increase during the lifetime of the pulse. Such photoinitiation of explosion can be achieved with a powerful infrared pulse and corresponds to a physically realizable case.

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Figure 1. Types of Real and Hypothetical Radiative Pulses That Can Explosively Modify A Quasi-Steady Sample of an Unstable Compound

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3. A photodissociative pulse, such as \mathfrak{F}_3 , is represented by a straight horizontal line. If the energy of the pulse is sufficient, the change in the originally stable system is characterized by a large increase in the reactive intermediate concentration, and the resultant unstable trajectory leads to explosion. Physically, such a case can only be approximated.
4. A pulse such as \mathfrak{F}_4 , containing ultraviolet and other wavelengths, is represented by a straight, diagonal line. If the energy of the pulse is sufficient, the change in the originally stable system is characterized by both a temperature increase and an increase in the reactive intermediate concentration and the resultant unstable trajectory leads to explosion.

Ultraviolet radiation, or a combination of ultraviolet and long wavelength radiation, leads to both photodissociation and thermalization of the incident radiation. Physically, however, the arbitrarily short pulse time can only be approximated.

5. A pulse such as \mathfrak{F}_5 (again with duration comparable to the response time), containing ultraviolet and other wavelengths, is represented by a curved line. The primary act of photoabsorption (creation of a pre-dissociated state) leads both to photodecomposition and to thermalization of the incident photon's energy. Both T and $[B]$ increase and, if the properties of the pulse are adequate, the change in the originally stable system leads to an unstable trajectory and explosion. Such photoinitiation of explosion can be achieved with a powerful ultraviolet pulse, or some mixture of ultraviolet-containing wavelengths. Such a case is possible when an unstable compound is suddenly injected into the radiative environment of a rocket engine. This also is the case

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characterizing the well known flash photolysis experiments. Of course, photolysis which does not lead to explosion is represented by the stable trajectories which lie below the separatrix.

Of the above five cases, (2) and (5) represent systems which can be physically realized. There is a continuum of possible $(\Delta T, \Delta B)$ values associated with the possible pulses that can just barely drive the originally stable system onto an unstable trajectory. Clearly, the energy of the flash does not in itself characterize photoignition, for any given unstable system. Spectral distribution plays a role. Also, there exists an infinitude of unstable trajectories. Consequently, it is apparent, for the case of flash photolysis experiments, that the experimentally observed (T, B) trajectories seen after cessation of the flash, are not necessarily independent of the initiator. It is also true, however, that as the unstable trajectories converge to the singularity associated with the final products in equilibrium, that the (T, B) values along the trajectories converge, in time.

Implicit in the representation presented in Fig. 1 is the approximation that the initial reactant concentration has not been significantly changed during the time period of the ultraviolet flash. This may not be a suitable approximation in all cases.

In the next section, the calculated time behavior of temperature and intermediate species concentrations is presented for a given case of ultraviolet irradiation and explosion of hydrazine.

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V. THE PHOTOCHEMICAL STEADY STATE AND EXPLOSIONS

Classically,²⁻³ thermal explosion theory considers the quasi-steady state of a sample of an unstable compound to be at a temperature T_1 (Fig. 2a) when the heat release rate and heat loss rate of a reaction are plotted versus temperature. T_2 corresponds to an unstable point for which the heat loss and heat generation rates are equal. Explosion is taken to occur when T_1 and T_2 merge, as shown in Fig. 2b. In modifying such a representation for the presence of a steady state photodissociative flux, the heat release rate function must account for both the thermal and kinetic effects of the photoabsorption events. Here, either a photochemical quasi-steady state is achieved, or explosion occurs (Case (B) of Section III). Again, explosion is taken to occur when the heat loss rate and heat generation rate functions are just tangent (as in Fig. 2c). For the case of a cylindrical sample of hydrazine, the kinetic scheme discussed in Appendix I may be used to obtain the following values of $[\text{NH}_2]$ and T at the photochemical steady state condition:

$$[\text{NH}_2]_{\text{SS}} = \left[\frac{k_v + k_1[\text{N}_2\text{H}_4]}{k_2} + \left(\frac{k_5}{k_7} \right) [\text{N}_2\text{H}_4] \right]$$

$$T_{\text{SS}} = T_b + \left(\frac{(\Delta H_c) d^2 [\text{N}_2\text{H}_4]}{8\lambda} \right) \left\{ k_v \left[\frac{E_v - E_D}{2(\Delta H_c)} + 1 \right] + k_1[\text{N}_2\text{H}_4] + \frac{k_2 k_5}{k_7} [\text{N}_2\text{H}_4] \right\}$$

At the explosion condition, $[\text{NH}_2]_s$, $[\text{NH}]_s$, and T_s depend upon the radiative field. Of course, the critical bath temperatures are not the same, for any two different radiative fields, each corresponding to an explosion condition.

On the other hand, a more general (phase plane) analysis that accounts for both kinetic and thermal considerations may be expected to yield more reliable results.

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Equations (16) and (17) may be employed, together with the consideration that the nodal point and the saddle point of the phase plane are coincident⁵ at the explosion limit to deduce the explosion limits of a cylindrical sample of irradiated hydrazine:

$$\left[(h_2 F) \frac{\partial}{\partial T} \left\{ \begin{array}{c} (k_v - k_2) \\ + \left(\frac{k_1 k_7 + k_2 k_5}{k_7} \right) \end{array} \right\} \right]_{\substack{[NH_2]_{PS}, \\ T_{PS}}} = - \left[\frac{\partial}{\partial T} \left\{ \begin{array}{c} (E_v - E_D)k_v + k_1 F h_1 + k_5 C_{PS} h_5 \\ + k_6 A_{PS} h_6 + k_7 \left(\frac{AC}{F} \right)_{PS} h_7 + h_2 k_2 B \\ - \frac{16\lambda(T - T_B)}{d^2} \end{array} \right\} \right]_{\substack{[NH_2]_{PS}, \\ T_{PS}}}$$

A similar expression may be written for the case of ozone.

The classical representation is not suited for prescribing the time-dependent behavior of a sample of an unstable compound during ultraviolet photolysis. This is particularly true when photolysis occurs during a time period that is comparable to the induction time of the reaction or when a significant fraction of the initial reactant concentration is consumed during the early portion of the photolysis. For such a situation, direct integration of the time-dependent equations is necessary.

This is discussed in the next sections, first for the mixed hydrazine family of reactants, then for ozone.

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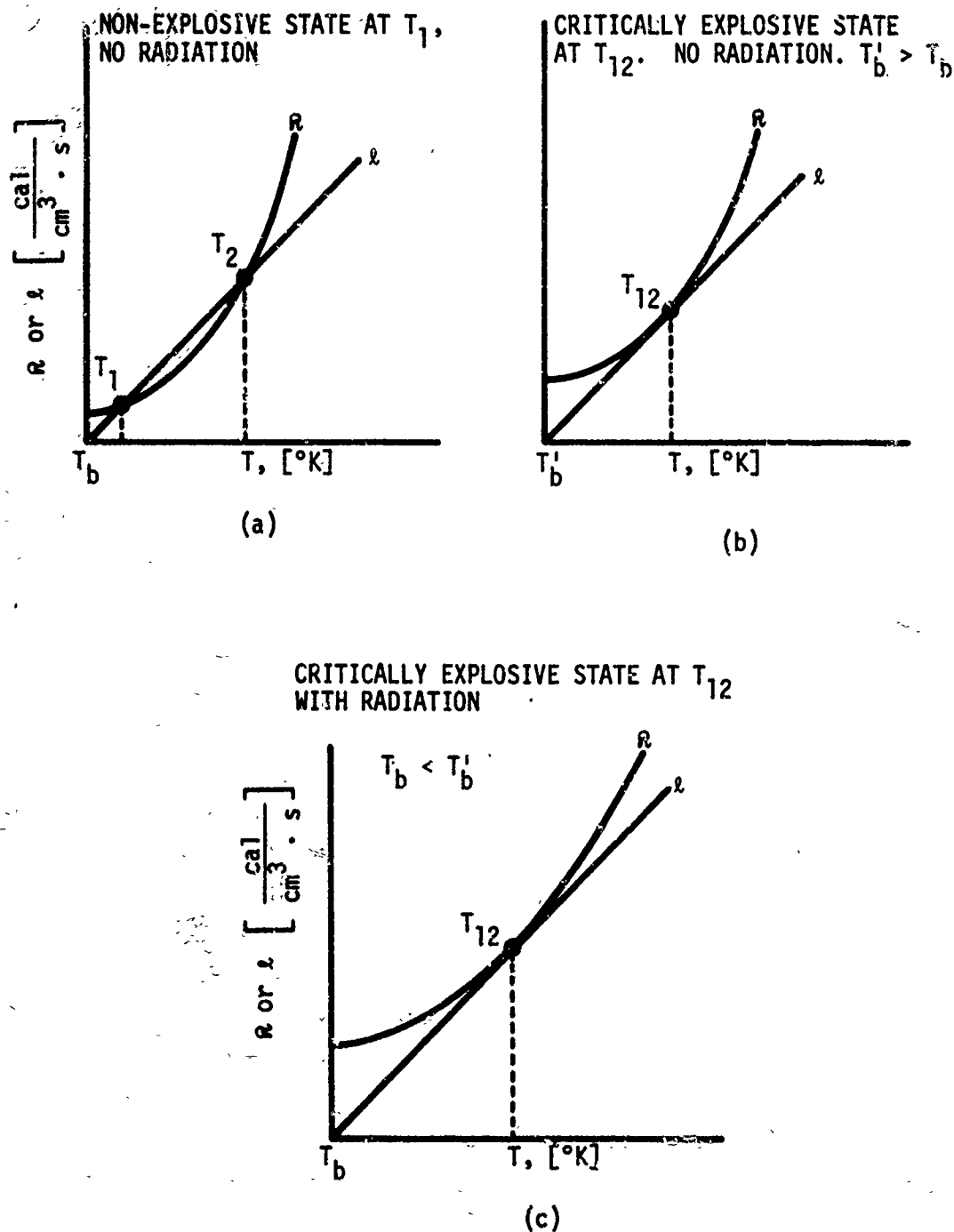


Figure 2. Thermal Theory Comparison of (a) Ordinary Quasi-Steady State
(b) Critical Explosion Condition Without Radiation
(c) Critical Explosion Condition With Radiation

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VI. CALCULATED TEMPORAL BEHAVIOR OF T, NH, NH₂, N₂H₃, AND N₂H₄ FOR THE ULTRAVIOLET PHOTOLYSIS OF HYDRAZINE

Employing the kinetic scheme given in Appendix I we examine some trajectories resulting from the ultraviolet flash irradiation of initially quasi-steady samples of hydrazine. Similar calculations can be carried out for other members and combinations of members of the mixed hydrazine family of fuels. The conservation equations are:

$$\frac{dT}{dt} = \frac{[N_2H_4]}{\rho c_p} \left\{ \begin{aligned} &k_v(E_v - E_D) + k_1[M]h_1 + k_2[NH_2]h_2 \\ &+ \frac{[N_2H_3]}{[N_2H_4]} \left([M]k_5h_5 + [NH_2]k_7h_7 \right) + k_6[NH]h_6 \end{aligned} \right\} - \left(\frac{16\lambda(T - T_b)}{\rho c_p d^2} \right) \quad (16)$$

and

$$\frac{d}{dt} [NH_2] = [N_2H_4] \left\{ \begin{aligned} &2(k_v + k_1[M]) + (k_5[M] - k_7[NH_2]) \left(\frac{[N_2H_3]}{[N_2H_4]} \right) \\ &+ k_6[NH] - k_2[NH_2] \end{aligned} \right\} \quad (17)$$

$$\frac{d}{dt} [NH] = k_5[N_2H_3][M] - k_6[N_2H_4][NH] \quad (18)$$

$$\frac{d}{dt} [N_2H_3] = (k_2[NH_2] + k_6[NH]) [N_2H_4] - (k_5[M] + k_7[NH_2]) [N_2H_3] \quad (19)$$

$$- \frac{d}{dt} [N_2H_4] = [N_2H_4] \{ k_v + k_1[M] + k_2[NH_2] + k_6[NH] \} \quad (20)$$

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A. STEADY STATE IRRADIATION

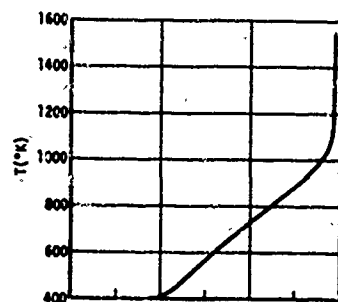
Figure 3 shows T , $[N_2H_4]$, $\frac{d}{dt}[N_2H_4]$, $[NH]$, $[NH_2]$, and $[N_2H_3]$ as a function of time for the case of $[N_2H_4]$ photolysis at 2250 Å, where $T_b = 400^\circ K$; an initial $[N_2H_4]$ value corresponding to 100% gaseous hydrazine at a density of $5.69 \times 10^{-3} \text{ gm/cm}^3$; $d = 0.60 \text{ cm}$; $E_D = 57,100 \text{ cal/mole}$; and a steady state k_v of 303 s^{-1} , corresponding to a local ultraviolet flux deposition rate of $6.36 \times 10^3 \text{ cal/cm}^2/\text{s}$. The k_v value goes from zero at 90 microseconds to its steady state value of 303 s^{-1} in 20 microseconds. Focusing our attention on the behavior of T and $[NH_2]$ we see that the initiating process is very much like that indicated by β_5 , of Fig. 1. Once an explosive trajectory is reached, the behavior in the $[T]$ vs $[NH_2]$ plane of the system is virtually independent of the (steady state) existence of the ultraviolet source. This has been confirmed by computations in which the flash is cut off at times such as 260 microseconds, 270 microseconds, 280 microseconds, etc. At substantially shorter times, of course, cut-off of the flash leads to a non-explosive condition of the reacting medium. Of particular interest is the approximately steady-state behavior of both $(d/dt)[N_2H_4]$ and $[NH_2]$ in the neighborhood of 200-250 microseconds, immediately before all the derivatives "blow up." Also to be noted is that during the period from 100 to 250 microseconds the reaction process can be regarded as quasi-steady as far as $[NH_2]$ and $(\frac{d}{dt})[N_2H_4]$ are concerned and a small but significant fraction of the reactant is used up before this quasi-steady state is destroyed. Thus, the explosive behavior (in the neighborhood of 250-300 microseconds) follows the destruction of the photochemical quasi-steady state of the reaction rate and $[NH_2]$. This occurs in the neighborhood of $900^\circ K$ (see Fig. 3), some $350^\circ K$ higher than classical analysis predicts (as discussed in Section VI). The results of classical analysis of the photochemical steady state are indicated in Appendix III.

B. EFFECT OF PULSE DURATION

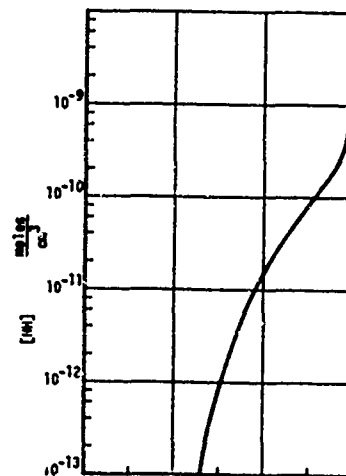
In the previous section, we discussed the irradiation of a N_2H_4 sample by a square wave pulse. This feature is reflected by the fact

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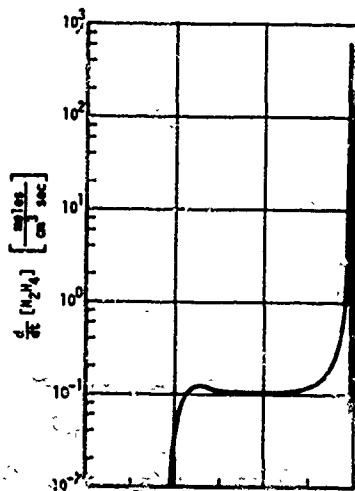
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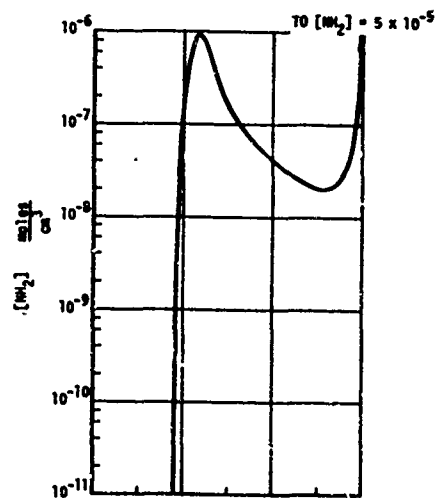
(a) Temperature vs time



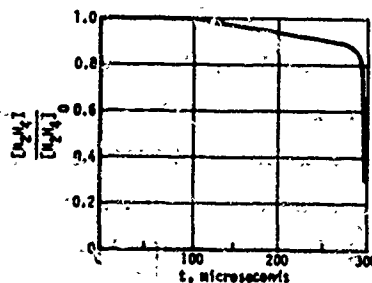
(d) [NH] vs time



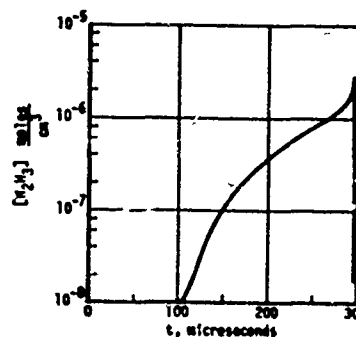
(b) Reaction rate vs time



(e) [NH₂] vs time



(c) Reactant Concentration vs time



(f) [N₂H₃] vs time

Figure 3. Explosive Behavior of Hydrazine During Ultraviolet Photolysis (calculated).

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that $k_v = 303 \text{ s}^{-1}$ throughout the time interval of primary interest. Inasmuch as k_v is proportional to the local rate of absorption of u.v. photons, a pulsed (finite) radiative source corresponds to a k_v that goes from zero to a finite value and then back to zero all within the time interval of interest. The effect of such pulses has been investigated. In the tabulation given below, the half-life of the N_2H_4 sample is compared with the time at which the value $k_v = 303 \text{ s}^{-1}$ is suddenly taken to zero (pulse cut-off).

Pulse Cut-off	Sample Half-Life
Microseconds	Microseconds
Steady pulse	295.6
294.0	295.6
290.0	296.4
270.0	335.5
240.0	≈ 500

As the pulse is cut off at shorter and shorter times, the sample half-life increases by orders of magnitude. Of course still shorter pulses of the same energy lead to half-lives that correspond to the "slow decomposition" process. In steady-state analyses, this is the "non-explosive" regime.

C. EFFECT OF SPECTRAL PROPERTIES OF THE PULSE

Given a pulse of fixed power and duration, it is expected that the spectral distribution of the pulse energy will influence the temperature-composition history of the sample. This temporal behavior depends very greatly on the chemical nature of the compound under consideration. For the case of hydrazine we have performed calculations of these trajectories for various spectral distributions of continuous pulses at constant total power corresponding to $k_v = 303 \text{ s}^{-1}$.

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Cases	Fraction of Pulse Power Thermalized	Fraction of Pulse Power into Dissociation	Sample N_2H_4 Half-Life (microseconds)
1 (hypothetical)	0.00	1.00	270
2 (the treated case)	0.55	0.45	295
3 (a possible case)	0.75	0.25	337
4 (a possible case)	0.90	0.10	357
5 (a possible case)	1.00	0.00	373

For smaller values of radiative flux density, the calculated spread of sample half-life increases sharply, reflecting the differences in trajectory times close to the separatrix (Fig. 1). Also to be noted is the fact that Case 5 corresponds to a purely thermal pulse (\mathcal{F}_2 of Fig. 1) but that Cases 1-4 all lie in the quadrant associated with \mathcal{F}_5 (Fig. 1).

D. EFFECT OF SAMPLE DIAMETER

In steady-state explosion theory, the critical conditions for explosion depend on the thermal losses for the system, and therefore on the tube diameter. By the same token (Eq. (16)) the rate of temperature rise and the sample half-life of an irradiated sample also depend on the sample's diameter. The following results are obtained for a constantly irradiated sample under conditions previously employed:

Sample Diameter cm	Sample Half-Life Microseconds
0.600	295.6
0.060	296.5
0.006	485.0

The sample diameter has very little effect on the sample half-life for sizes greater than a few hundred microns. For explosive trajectories involving longer half-lives (and smaller k_v values), the effect of sample size becomes progressively greater.

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VII. MONOMETHYLHYDRAZINE AND UNSYMMETRICAL DIMETHYLHYDRAZINE

Both UDMH and MMH are easier to dissociate than N_2H_4 .¹⁶ Consequently, both the heats of reaction and the rate constants given for the N_2H_4 scheme (Appendix I) must be modified. The primary modifications are indicated below:

	N_2H_4	MMH	UDMH
E_D	57,100 cal/mole	51,900 cal/mole	49,600 cal/mole
E_1	57,100 cal/mole	51,900 cal/mole	49,600 cal/mole
E_5	18,000 cal/mole	12,800 cal/mole	10,500 cal/mole
$(E_v - E_D)$	69,400 cal/mole	74,600 cal/mole	76,900 cal/mole
k_1	$10^{19} \exp \left[-\frac{57,100}{RT} \right]$	$10^{19} \exp \left[-\frac{51,900}{RT} \right]$	$10^{19} \exp \left[-\frac{49,600}{RT} \right]$
k_5	$10^{12} \exp \left[-\frac{18,000}{RT} \right]$	$10^{12} \exp \left[-\frac{12,800}{RT} \right]$	$10^{12} \exp \left[-\frac{10,500}{RT} \right]$

Although the optical extinction coefficients for the above three reactants are approximately equal, the lower E_D is the greater the fraction of an absorbed u.v. photon's energy which goes directly into raising the sample's temperature. Additionally, the lower E_D is the higher k_1 and k_5 are. Thus, from both a thermal and photochemical point of view, UDMH is the most reactive of the three reactants and N_2H_4 the least reactive. No consideration is given here to possible heterogeneous reactions.

A test of the kinetic scheme and rate constants was made for the case of UDMH. Figure 4 shows a comparison of our calculated explosion limits with those observed by P. Gray and M. Spencer.¹⁴ Agreement appears good, particularly when one considers the unsuitable geometry (short cylinder) used by Gray and Spencer.

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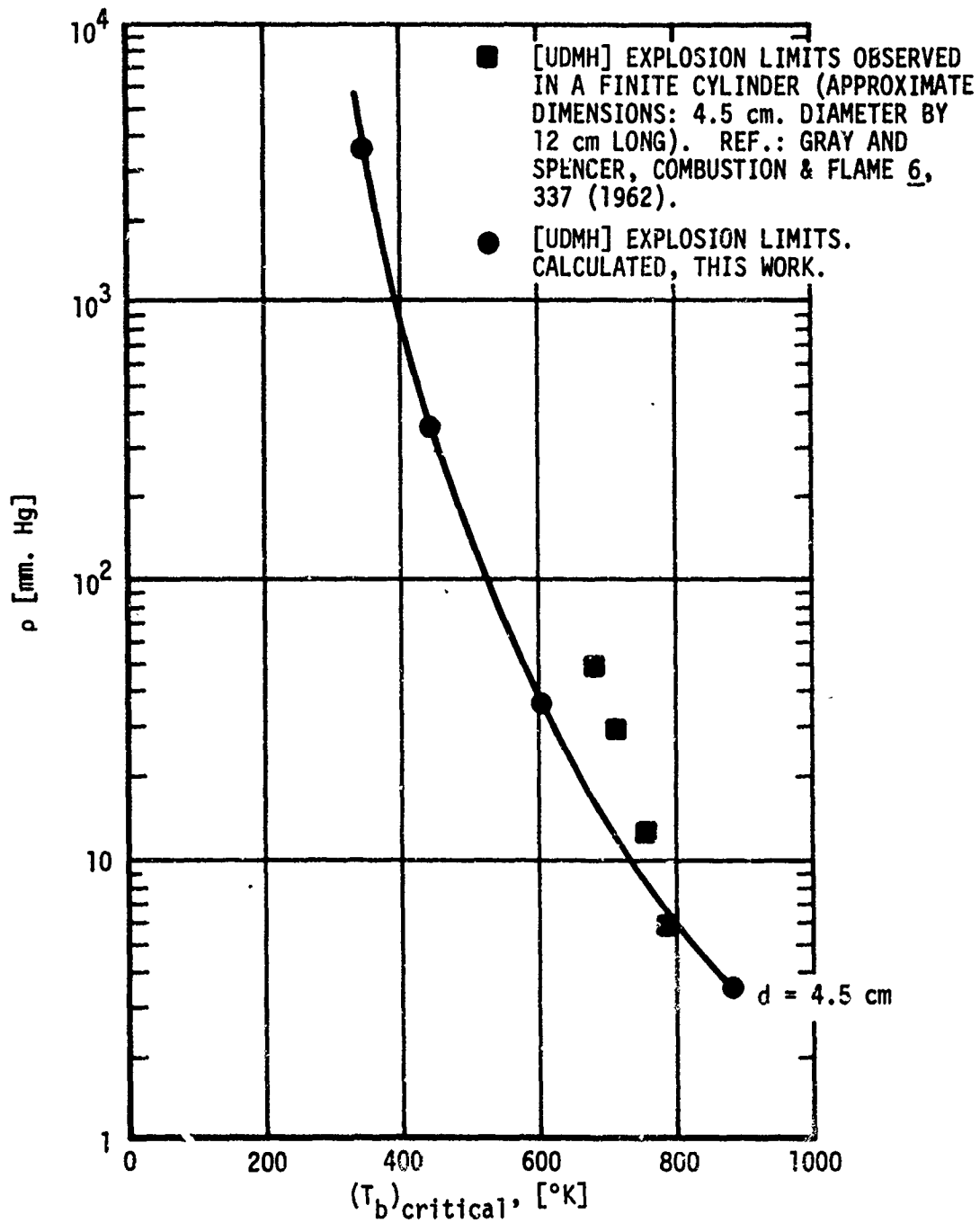


Figure 4. UDMH Explosion Limits

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For ambient conditions similar to those chosen for N_2H_4 , steady-state explosion limits were calculated for UDMH and MMH. For $p = 46$ atm, MMH (sample size of 0.6 cm diameter) becomes thermally unstable at an average sample temperature $411^\circ K$; for UDMH, this occurs at $361^\circ K$. As noted earlier, thermal instability does not necessarily assure a sharp thermal and pressure spike.

For the case of MMH at a bath temperature of $300^\circ K$, a steady-state local u.v. radiative flux density of 4.97×10^{-3} watt/cm² causes thermal instability. For the case of UDMH, 2.41×10^{-3} watt/cm² causes thermal instability.

Time-dependent calculations show that UDMH, in a strong u.v. radiative field, gives a thermal spike in a shorter time than MMH which, in turn, "explodes" in a shorter time than N_2H_4 . These conclusions are implied by the homogeneous gas phase kinetics noted previously and are demonstrated by the calculated results. These are indicated below.

For equal initial molar densities (1.77×10^{-4} moles/cm³), $T_b = 400^\circ K$, $d = 0.6$ cm, and a $k_v = 303$ s⁻¹ for $t \geq 110$ μs , the following results are obtained:

	Sample Half-Life (microseconds)
N_2H_4	295
UDMH	148
MMH	184

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VIII. SOME SUMMARY COMMENTS ON THE BEHAVIOR OF UNSTABLE MIXED HYDRAZINE
REACTANTS IN AN ENGINE ENVIRONMENT

Based on our experimental observations as well as our detailed calculations of sample half-lives, explosive trajectories and explosion limits for N_2H_4 , MMH, and UDMH in the presence and absence of radiative fields (both U.V. and I.R.) we make several observations:

1. In the absence of a radiative field the explosion limits of N_2H_4 , MMH, UDMH and 50%-50% mixtures of N_2H_4 -UDMH occur at temperatures ($\lesssim 600^\circ K$) that are easily achieved in the "low temperature" regimes of engines. However, the rate of temperature (and pressure) rise in the neighborhood of the explosion conditions determines the apparent stability of a compound in a piece of hardware. Our experiments and calculations show that this rate of rise, for these compounds, is relatively slow in the neighborhood of $600^\circ K$. The behavior for the case of N_2H_4 is typical. Just below $600^\circ K$ (Appendix III) a sample of N_2H_4 may become explosively unstable (the steady-state explosion condition is satisfied). However, a really short sample half-life (calculated to be about 50 μs) corresponds to a gaseous sample at $900^\circ K$. Of course, a reactant half-life that is "short" corresponds to a "short induction period"; a "long" half-life corresponds to a "long induction period." Thus, in the absence of additional external heat inputs, an explosively unstable sample at $600^\circ K$ (above the steady-state explosion limits) has a sample half-life of many milliseconds (and perhaps much longer). As a result of this behavior (confirmed both experimentally and analytically), the engine designer can usefully employ hydrazine at temperatures that are higher than those associated with the explosion limits.

2. In the presence of a weak, steady-state radiative field, the explosion conditions (associated with the photochemical steady state) are achieved at a lower temperature than normal. Again, because of the long reactant half-lives at the explosion condition, a reactant sample disappears slowly (over a period of many milliseconds, or even seconds and minutes).

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Rapid decomposition does not occur until the neighborhood of 900°K is achieved. Thus, the weak radiative field does not really affect the salient feature of the system - namely that the engine design can usefully permit the flow of the reactant in the combustion chamber at a temperature above the explosion limit, for several milliseconds, before stable combustion processes consume the reactant.

3. In the presence of a strong, steady-state radiative field, the explosion conditions (associated with the photochemical steady state) are achieved at a still lower temperature. Again, because of the relatively slow decomposition behavior of N_2H_4 at these temperatures ($< 600^{\circ}\text{K}$), the half life of the sample can be short (less than a millisecond) only if the radiative field is sufficiently strong to drive the sample temperature to some 900°K in a matter of a few hundred microseconds. For strong radiative fields (Section VI), this is indeed possible. In fact, the infrared radiation of an engine environment is almost as effective as the photochemically significant ultraviolet radiation, for the case of hydrazine (Section VI-C). (This is not true for the case of ozone.) Inasmuch as rocket engines are strong sources of infrared, it is clear that this source of energy must be included in the engine designer's calculation of the temperature history of a sample of an unstable compound.

4. It is incorrect for an engine designer to estimate the temperature rise of a reactant sample (due to external heat sources, radiative or other) without including the self-heating effects due to the exothermic decomposition of the sample. Thus, the considerations employed here, in deducing explosive trajectories and sample half-lives, are necessary ones. Where other than radiative terms play a role in this temperature rise, these new terms must be included also in the time dependent energy equation.

A particularly valuable lesson to derive from the behavior of this class of reactants is that the calculation of a simple steady-state explosion limit, in itself, is not adequate to describe the stability and

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behavior of a reactant sample in an engine environment. Thus, for the case of the hydrazine family of reactants, the "thermal instability" of the liquid does not lead to a sharp pressure pulse such as that which is associated with a sample half-life of a few hundred microseconds. Rather this "thermal instability" results in an increased rate of vaporization of the unstable liquid (drop or film), due to the internal heat generation. This occurs in a temperature regime where the gas phase is not explosively unstable. Consequently the accelerated vaporization process (which may give rise to a "popping" effect) acts as a heat sink, fixing an upper limit on the temperature of the liquid sample. Any destructively large pressure pulses that may then result must be associated with the later temperature history of the resulting gas phase sample. The engine designer may then determine, from the time dependent calculations (such as those performed here), how much time is available for the resultant gaseous sample to be mixed and burned, if the explosive behavior of the reactive gas is to be avoided. For the case of the hydrazine class of reactants, this is easily achieved in the neighborhood of 600°K (sample half-lives of many milliseconds) and difficult to achieve in the neighborhood of 900°K (sample half-lives of a few hundred microseconds or less).

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IX. CALCULATED BEHAVIOR OF T, O, O^{*}, O₂, O₂^{*}, AND O₃ FOR THE ULTRAVIOLET PHOTOLYSIS OF OZONE

Following the analytic approach previously discussed for the time-dependent explosive behavior of the mixed hydrazine family of reactants, we consider the appropriate equations for the case of ozone. Employing the kinetic scheme discussed in Appendix II and setting

$$[O_3] = F, [O_3]_{\text{initial}} = F_o, [O] = A_1, [O^*] = A_e, [O_2^*] = B_e$$

we may write the rate equations (appropriate to high initial ozone concentrations):

$$-\left(\frac{dF}{dt}\right) = k_v F + k_1 F F_o + k_2 A_1 F + k_3 F A_e + k_4 F B_e - \frac{3}{2} k_6 A_e (F_o)(F_o - F) \quad (21)$$

$$\left(\frac{dA}{dt}\right) = k_1 F F_o - k_2 F A_1 \quad (22)$$

$$\left(\frac{dA_e}{dt}\right) = k_v F + k_4 F B_e - k_3 F A_e - k_6 A_e F_o \left[\frac{3}{2}(F_o - F)\right] \quad (23)$$

$$\left(\frac{dB_e}{dt}\right) = k_3 A_e F - k_4 B_e F - k_5 B_e F_o \quad (24)$$

The energy equation yields

$$\frac{dT}{dt} = \frac{F}{\rho c_p} \left[\begin{aligned} &K_v(E_v - E_D - E_e) + k_1 F_o h_1 + k_2 A_1 h_2 \\ &+ k_3 A_e h_3 + k_4 B_e h_4 + k_5 B_e \left(\frac{F_o}{F}\right) h_5 \\ &+ k_6 \left(\frac{F_o}{F}\right) \left(\frac{3}{2}\right) (F_o - F) A_e h_6 \end{aligned} \right] - \left[\frac{16\lambda(T - T_b)}{\rho c_p d^2} \right] \quad (25)$$

Where assumption of a photochemical steady state is acceptable, the energy equation is:

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$$\rho c_p \left[\frac{dT}{dt} \right]_{ss} = \left[\left(- \frac{dF}{dt} \right)_{ss} \cdot \Delta H_c + k_v F (E_v - E_D - E_e) \right] - \left[\frac{16\lambda (T - T_b)}{d^2} \right] = R - L \quad (26)$$

and the steady state concentration and decomposition rate equations are:

$$[A_1]_{ss} = \frac{k_1 F_o}{k_2} \quad (27)$$

$$[A_e]_{ss} = k_v F \left[\frac{k_4 F + k_5 F_o}{k_3 k_5 F_o F + k_6 k_4 F_o F \left(\frac{3}{2} \right) (F_o - F) + k_6 k_5 F_o^2 \left(\frac{3}{2} \right) (F_o - F)} \right] \quad (28)$$

$$[B_e]_{ss} = \left[\frac{k_v k_3 F}{k_3 k_5 F_o + k_6 F_o \left(\frac{3}{2} \right) (F_o - F) \left(k_4 + k_5 \left[\frac{F_o}{F} \right] \right)} \right] \quad (29)$$

$$- \left[\frac{dF}{dt} \right]_{ss} = 2F \left[k_1 F_o + k_v \left\{ \frac{k_3 (k_4 F + k_5 F_o)}{k_3 k_5 F_o + k_6 F_o \left(\frac{3}{2} \right) (F_o - F) \left(k_4 + k_5 \left[\frac{F_o}{F} \right] \right)} \right\} \right] \quad (30)$$

Equations (26) to (30) are required for calculation of the explosive stability of the photochemical steady state.

Calculation of the time-dependent explosive behavior of a given ozone-containing sample requires consideration of Eqs. (21) - (25) inclusive.

Employing the kinetics and quantum yield data referred to in Appendix II, we obtain a selected list of enthalpies and rates:

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(a) Enthalpies: $E_d = 25,051$; $E_v = 101,000$; $E_e = 46,000$; $h_1 = -25,051$; $h_2 = 93,052$; $h_3 = 2,852$; $h_4 = 70,949$; $h_5 = 142,000$; $h_6 = 71,051$ cal/mole.

(b) Rates: $k_1 = 5 \times 10^{15} \exp[-24,000/RT]$; $k_2 = 3 \times 10^{13} \exp[-6000/RT]$; $k_3 = 10^{14} \exp[-\frac{3000}{RT}]$ cm³/mole-s; and $k_4 \sim k_2$ and, at 300°K, $k_5 \sim 10^{9.0}$ and $k_6 \sim 10^{5.9}$.

A. PHOTOCHEMICAL STEADY-STATE AND EXPLOSIONS OF OZONE

In considering the explosive disappearance of the photochemical steady state of ozone, we note that the temperature characterizing the rates of Eqs. (27) - (30) is not the bath temperature, T_b . Rather, it is the temperatures prescribed by simultaneous solutions of (27) - (29) in conjunction with the steady state assumption for the energy conservation equation:

$$\dot{q}''' = \rho c_p \frac{dT}{dt} = 0, \text{ or}$$

$$0 = \left[k_v [O_3] (E_v - E_d - E_e) + k_1 [O_3] [M] h_1 + k_2 [O_3] [O] h_2 + k_3 [O_3] [O^*] h_3 \right. \\ \left. + k_4 [O_3] [O_2^*] h_4 + k_5 [O_2^*] [O_3] h_5 + k_6 [O_3] [M] [O^*] h_6 \right] \quad (31)$$

$$- \left[\frac{16\lambda(T_1 - T_b)}{d^2} \right]$$

For values of k_v and T_b low enough to maintain a photochemical steady state that is far from explosion conditions, the approximation $T_1 \simeq T_b$ may be a good one. In general, and particularly in the neighborhood of an explosion condition, $T_1 > T_b$ and the approximation $T_1 = T_b$ is at its worst.

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Employing this thermokinetic consideration of the photochemical steady state, the steady-state values of $[O]$, $[O^*]$, $[O_2^*]$, and T_1 are deduced for a given system (size and pressure) for a range of bath temperatures and ultraviolet flux absorption rates. For a 2.50 cm diameter cylinder containing 100% ozone at a pressure of 0.05 atm, the results shown in Figs. 5-7 are obtained.

Examination of Figs. 5 and 6 shows that:

(a) $(T_1 - T_B)$ can be a kinetically significant quantity in the interpretation of a quantum yield experiment or an explosion limit experiment.

(b) The radiative field causes a decrease in the critical temperatures for explosion, $T_{1,2}$ and $T_{b,c}$ from those characterizing the case where $k_v = 0$

Figures (7a) to (7e) suggest the important roles played by $[O]$, $[O^*]$, and $[O_2^*]$ in definition of the photochemical steady state. At low temperatures and low k_v , the heat release rate is dominated by $[O_2^*]$. Both k_4 and h_4 are large.

In the neighborhood of the explosion limit, $d[O]/dk_v \gg d[O^*]/dk_v > d[O_2^*]/dk_v$. This implies that simple two-dimensional phase-plane representation of explosion limits may be adequate for representation of the photochemically influenced explosion limits of ozone. Thus, for constant k_v , only T and $[O]$ need be considered in the phase diagram. Of course, the roles of $[O^*]$ and $[O_2^*]$ in determining the steady-state concentration of $[O]$ must be included.

B. EXPLOSIVE TRAJECTORIES OF OZONE

The explosive trajectory for a given case of ozone irradiation can be calculated by use of Eqs. (21) - (25). This type of calculation is

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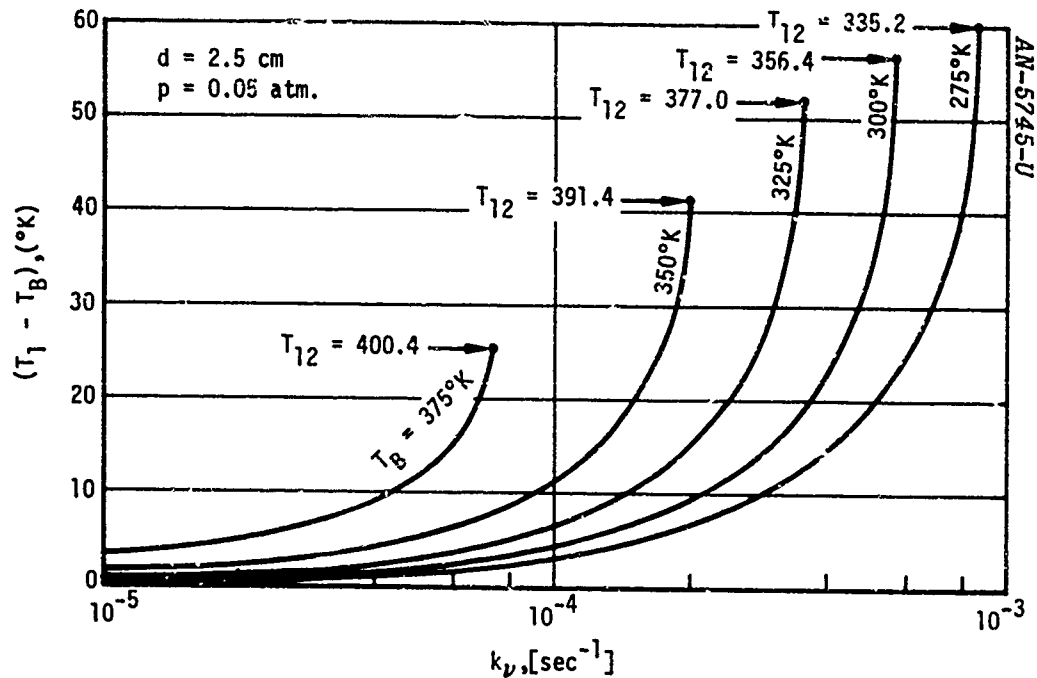


Figure 5. Photochemical Steady States for Ozone

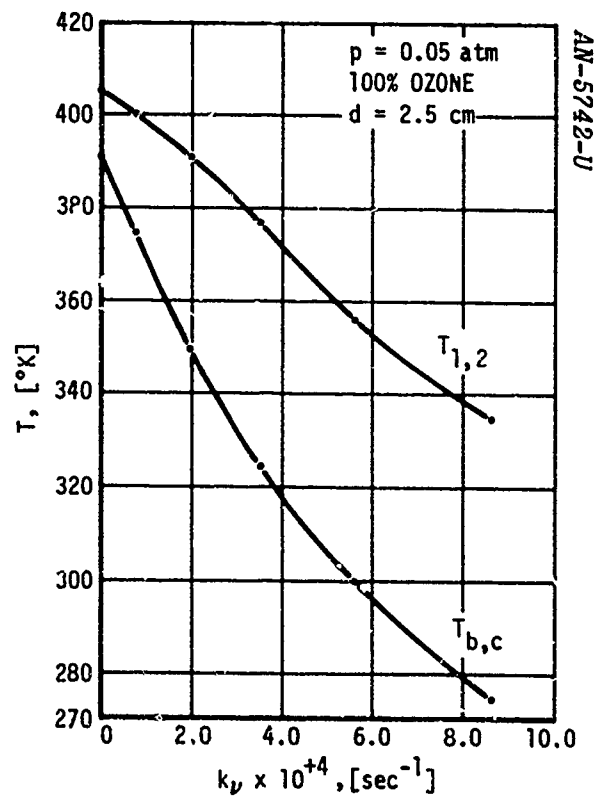


Figure 6. Critical Conditions for the Photochemical Steady State of Ozone

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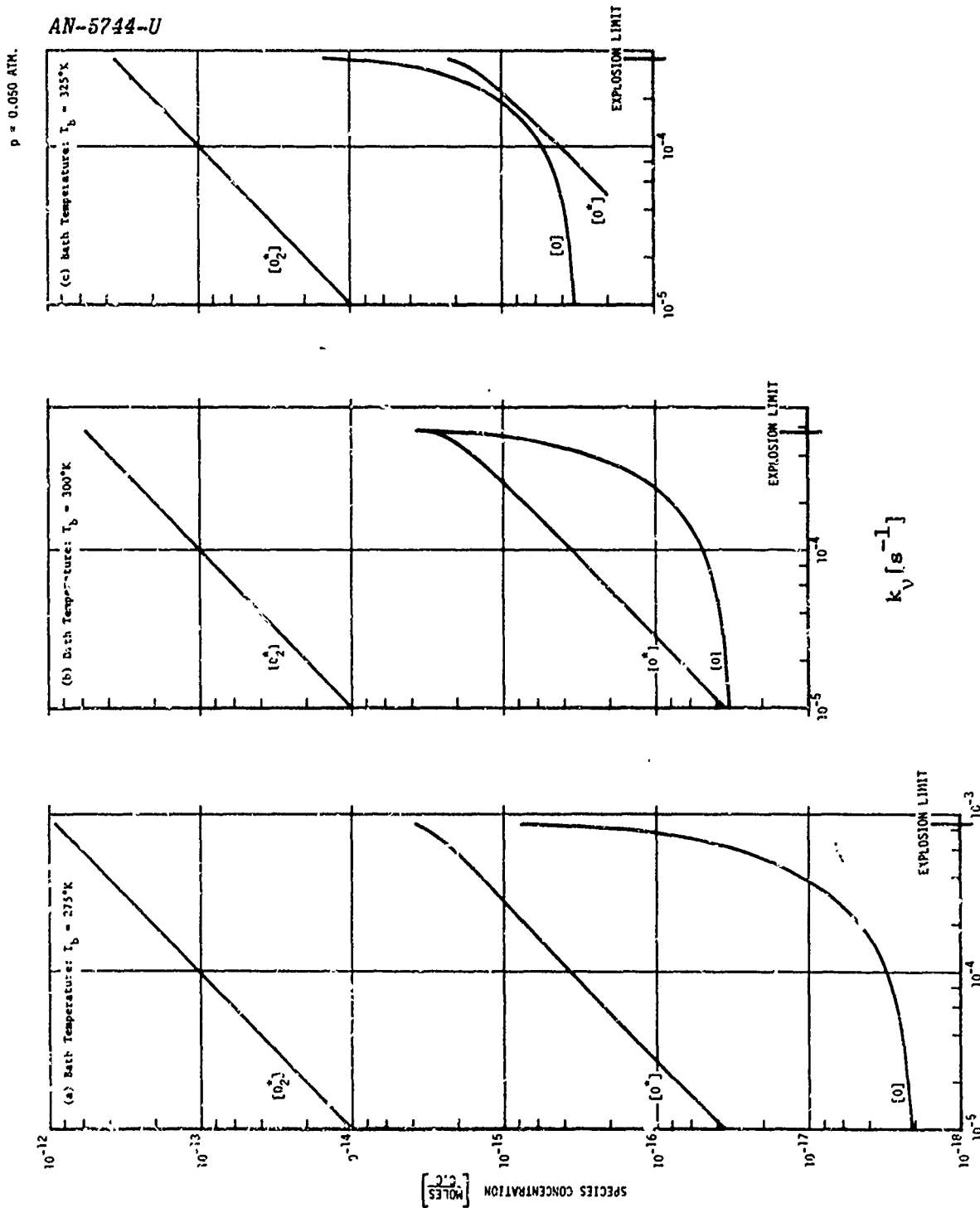
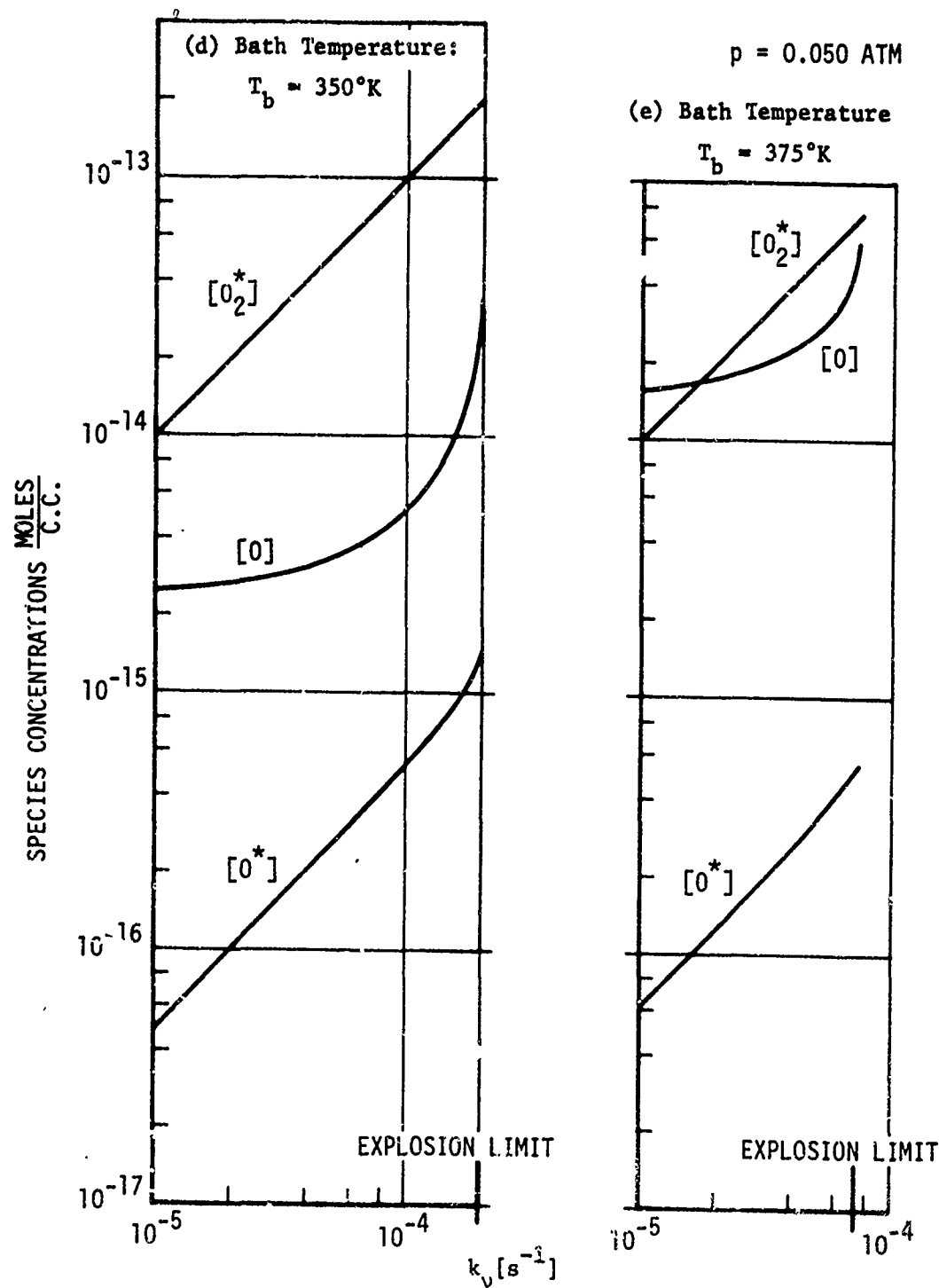


Figure 7. Calculated Species Concentrations for the Photochemical Steady State of a 25 mm Diameter Cylindrical Sample of Pure Ozone.

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shown for the case of gaseous ozone at a pressure of 1 atmosphere and an initial temperature of 300°K . A local radiative flux density of 100 watts/ cm^2 (u.v.) is assumed for the 6 mm diameter cylindrical sample.

The calculated trajectories are shown in Figs. 8a to 8e, where the time-dependent behavior of T , O_3 , O , O^* , and O_2^* are shown.

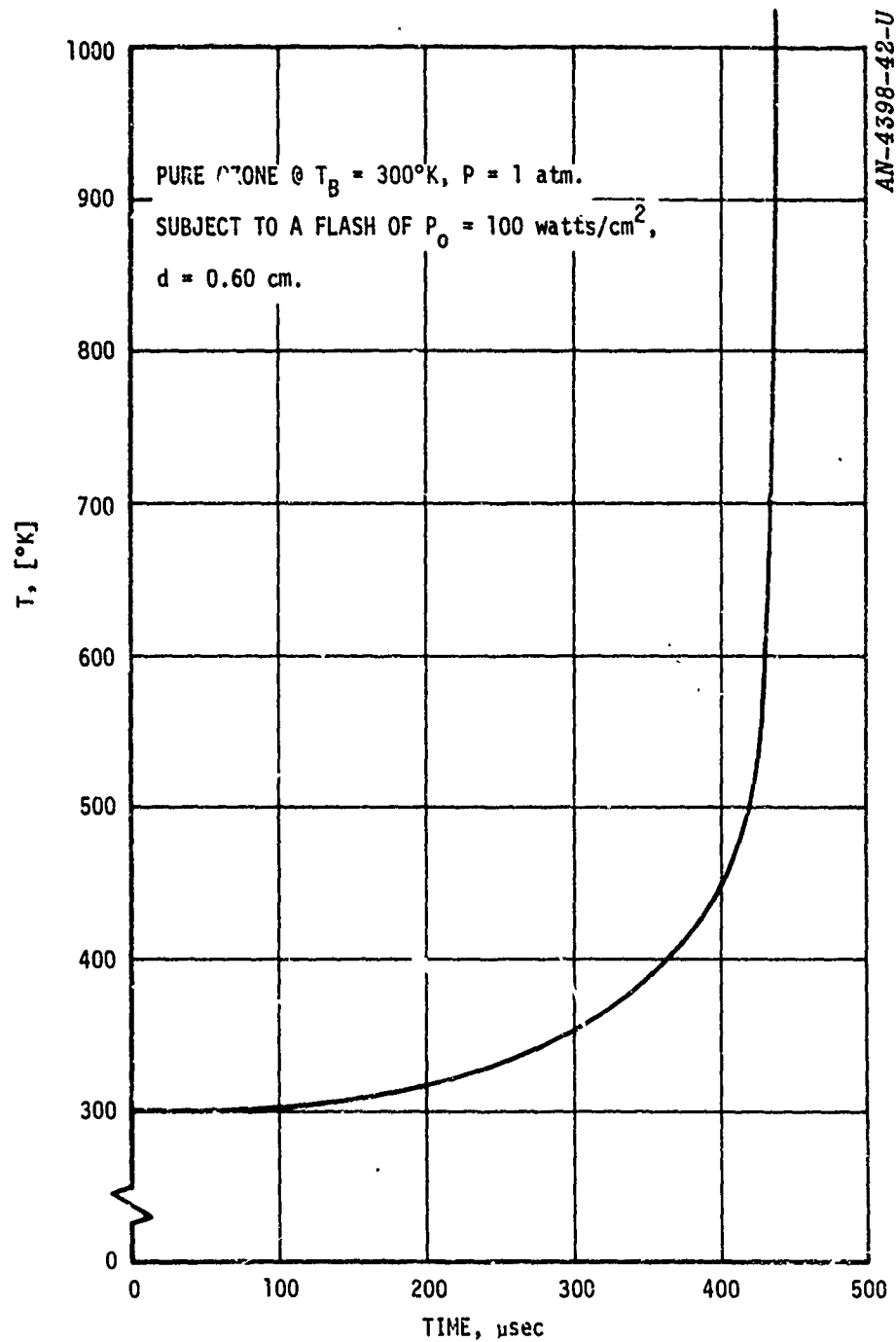
C. EFFECT OF FLUORINE ADDITIVES TO OZONE

It may be expected that the addition of quantities of fluorine to ozone will introduce new chain carriers, thereby sensitizing the decomposition of O_3 . Thus reactions involving F , F_2 , OF_2 , etc. play a key role in reduction of the temperatures associated with ordinary explosion limits for ozone. In addition, the photodissociation of F_2 and OF_2 (as well as O_3) in a rocket engine's radiative field suggests that trace amounts of F_2 or OF_2 will serve to sensitize O_3 , in a rocket engine environment.

On the other hand, large concentrations of F_2 in ozone introduce a stable sensitizer (F_2) at the partial elimination of the unstable reactant (O_3). Thus, at high concentrations of F_2 in O_3 (e.g., where $[\text{F}_2]/[\text{O}_3] \gg 1$) the temperatures associated with the ordinary explosion limits for ozone must increase. Thus, a prime goal of a study of explosion limits for $\text{O}_3\text{-F}_2$ or $\text{O}_3\text{-OF}_2$ mixtures is to define these explosion limits for a range of concentrations and radiative fields. It is clear, however, that for high fluorine concentrations (with ozone), adequate explosive stability of the $\text{O}_3\text{-F}_2$ system can be achieved. The detailed definition of these explosion limits is a matter for future study.

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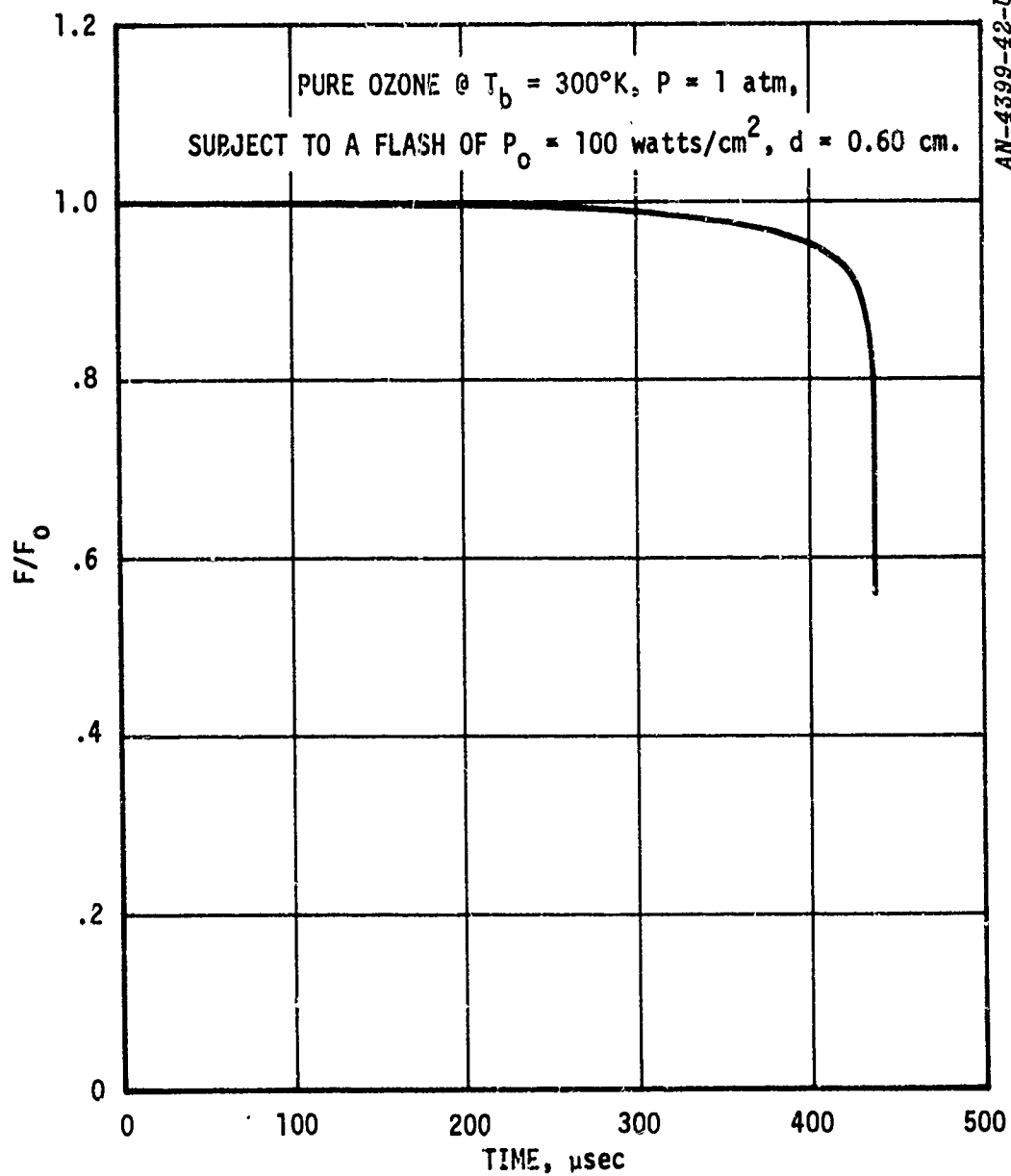


(a) Temperature vs Time

Figure 8. Temperature and Composition Histories for the Ultraviolet Photolysis of Ozone

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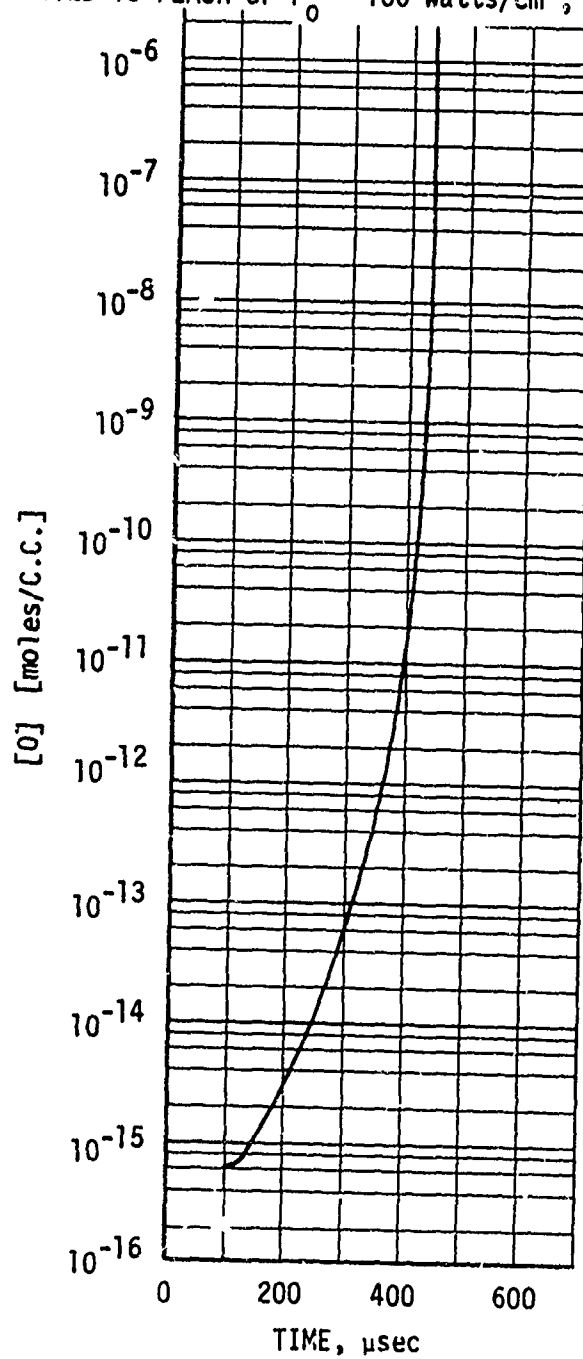


(b) Dimensionless Ozone Concentration vs Time
(Fig. 8 Cont'd)

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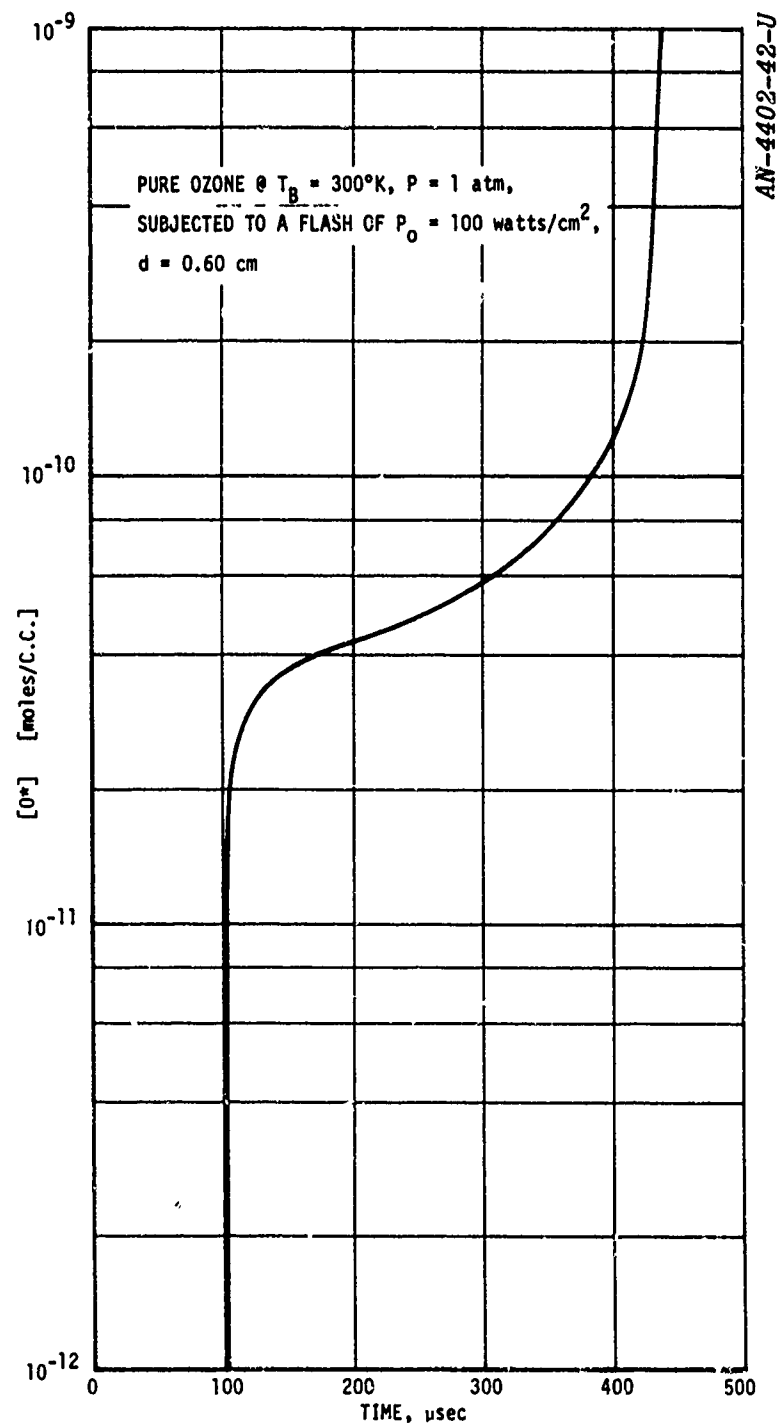
PURE OZONE, @ $T_B = 300^\circ\text{K}$, $P = 1 \text{ atm}$,
SUBJECTED TO FLASH OF $P_0 = 100 \text{ watts/cm}^2$, $d = 0.60 \text{ cm}$.



(c) $[O]$ vs time
(Fig. 8 cont'd)

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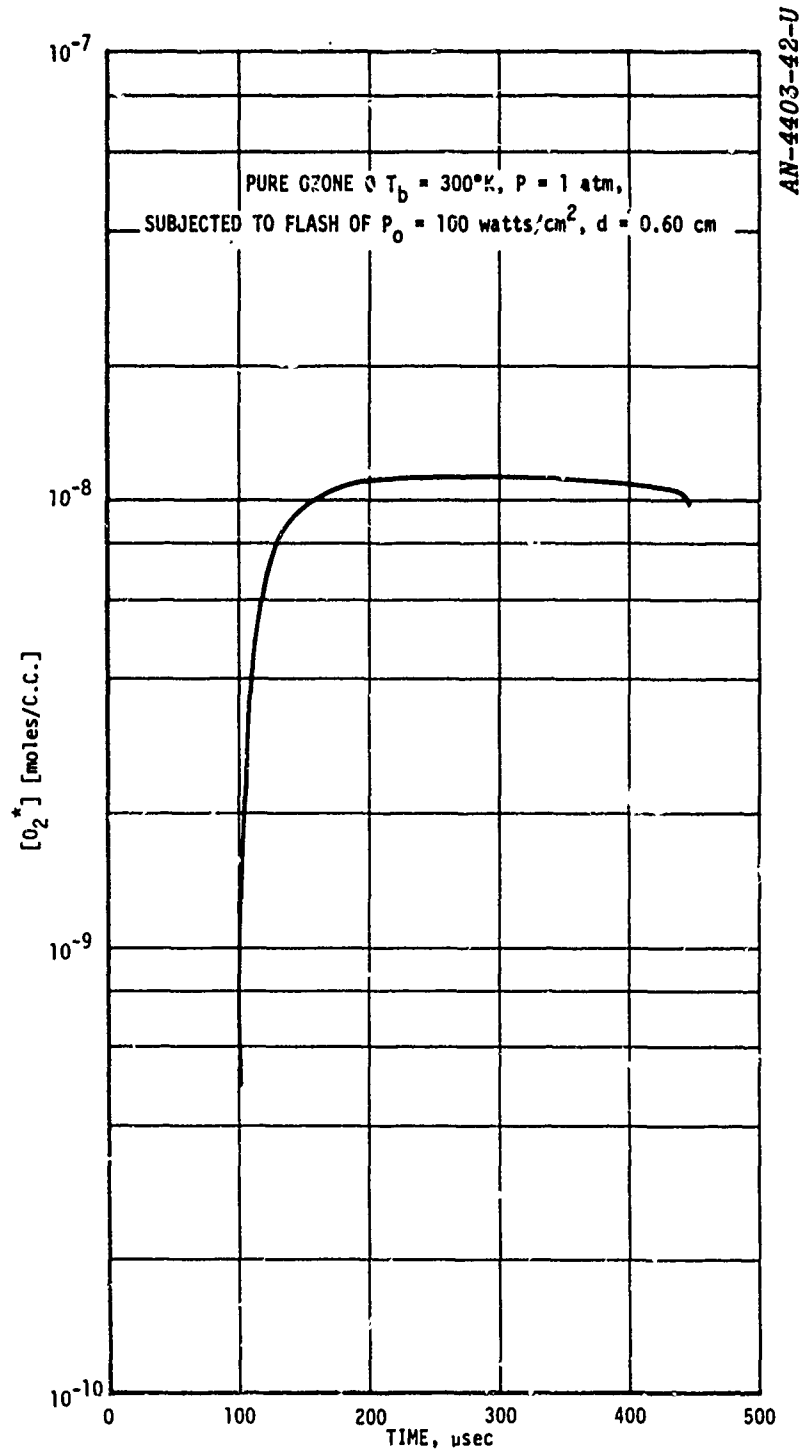
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(d) $[O^*]$ vs time
(Fig. 8 Cont'd)

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(e) $[\text{O}_2^*]$ vs time
(Fig. 8 cont'd)

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X. SOME CONCLUDING REMARKS

The roles of both steady and non-steady radiative fields in the explosive behavior of unstable compounds have been examined. The relations deduced have been employed in studying the explosive behavior of the mixed hydrazine family of reactants as well as the ozone system.

On the strength of these studies, it is concluded that:

(a) both hydrazine and ozone systems have their explosion limit conditions modified by the presence of radiative fields;

(b) on a per calorie basis, infrared radiation is not as effective in modification of the explosion limit as is photochemically significant radiation. This is particularly true for the case of ozone, where the explosion limit temperature, $T_{1,2}$, is greatly lowered by the photochemically induced concentrations of O^* and O_2^* ;

(c) ozone is (explosively) more sensitive to radiation than is hydrazine;

(d) explosive stability in a rocket engine environment is of prime interest. Reactant half-lives (ignition delays) of less than a few milliseconds are of major concern to the engine designer. We have shown that the half-life of an explosively unstable compound is a very sensitive function of the engine's radiative field, as well as a function of the usual kinetic and thermophysical constants;

(e) the full definition of the range of conditions over which a given unstable compound can be employed in a radiative environment can now be made by employing the deduced formulations to the deduction of reactant half-lives and explosion limits, for a range of radiative fields, pressures, temperatures, and sample sizes. Such detailed studies are necessary before rational use of ozone and ozone-fluorine propellant systems can be made by engine designers.

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XI. FUTURE STUDIES

Future studies of the explosive behavior of the ozone system are planned to include:

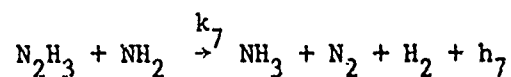
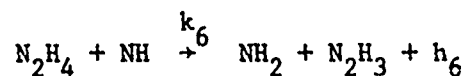
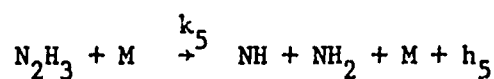
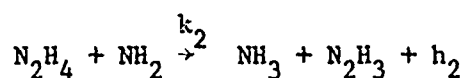
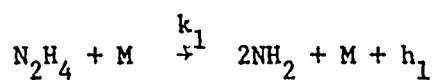
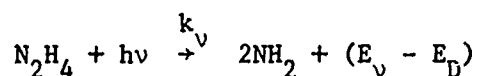
- (a) pressure as well as temperature and composition trajectories;
- (b) the effects of spectrally more complicated radiative fields (simultaneous u.v., visible, and infrared radiation); and
- (c) exploration of explosive trajectories associated with longer ozone half-lives (milliseconds).

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APPENDIX I

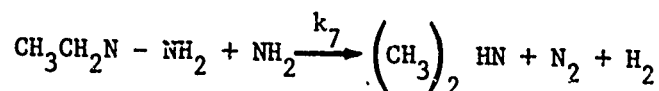
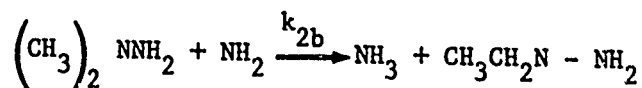
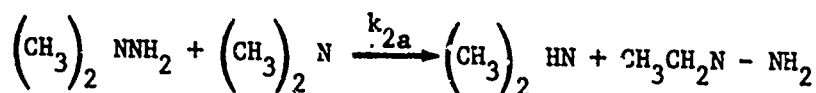
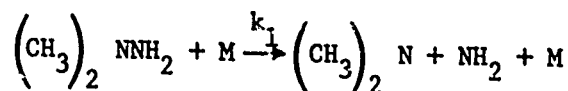
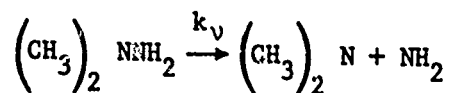
KINETICS OF DECOMPOSITION OF HYDRAZINE AND RELATED COMPOUNDS

There exists a substantial literature⁶⁻³⁸ concerning reaction rates and photochemical processes for Hydrazine, Monomethylhydrazine and Unsymmetrical Dimethylhydrazine. For purposes of this investigation, we require a kinetic scheme with knowledge of the rate constants, energetics of the individual steps, thermophysical properties of the reactants and products, ultraviolet quantum yields and the associated photochemical extinction coefficients. Although the literature is not fully adequate to our requirements, sufficient data are available to permit initial treatment of the problem. Accordingly, for the case of hydrazine, the scheme proposed by Eberstein and Glassman⁶ is simplified. Incorporating photodissociative processes in this modified scheme we write:



Further simplifications may be achieved if k_5 is taken to be small (step 5 is about as endothermic as step 1) and the other k - values modified to reflect this change. With this modification, appropriate schemes for MMH and UDMH decomposition can be represented in a manner that parallels that for N_2H_4 . Thus, the scheme proposed by Cordes⁷ for UDMH is modified:

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where $\left(\text{CH}_3\right)_2 \text{NH}$, NH_3 , N_2 , and H_2 are the product molecules.

A similar scheme may be written for MMH. In general, we write, for the hydrazine family of fuels (where F represents the fuel molecule):



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Tabulating for the three fuels involved:

Species	N_2H_4	CH_3HNNH_2	$(CH_3)_2NNH_2$
F	N_2H_4	CH_3HNNH_2	$(CH_3)_2NNH_2$
A	NH_2	CH_3HN	$(CH_3)_2N$
B	N_2H_3	$CH_3HN - NH_2$	$CH_3CH_2N - NH_2$
P_1	NH_3	CH_3H_2N	$(CH_3)_2HN$

where P_1 is an appropriate product molecule and A and B appropriate free radical intermediates. Where more complete kinetic representations are required for N_2H_4 , more complex (analogous) schemes also can be written for UDMH and MMH.

Clearly, there are deficiencies in our current understanding of the kinetics of the N_2H_4 family of fuels. The calculational techniques and phenomenological equations discussed in the text are, however, quite general. Thus, the general features deduced in the body of this work are relatively insensitive to modest modifications in the kinetics. This is in fact the case when the results of explosive behaviors of various members of the $[N_2H_4]$ family of fuels are compared.

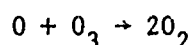
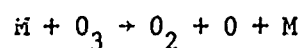
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APPENDIX II

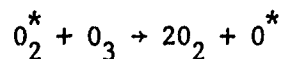
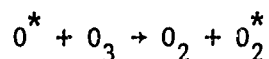
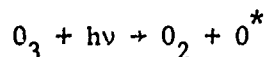
KINETICS OF DECOMPOSITION OF OZONE

A. OZONE KINETICS

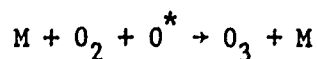
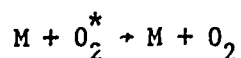
A rather extensive literature exists regarding the thermal and photochemical properties of ozone.⁴²⁻⁶⁷ The simplified kinetic scheme



represents the observed data quite well, for dilute ozone in the absence of photochemical sources.⁴ For concentrated ozone with photochemical sources, Semenov⁶⁰ has argued that the electronically excited states of O and O₂ (O* and O₂*, respectively) play a role through the reactions



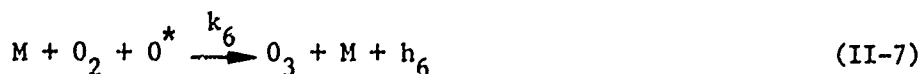
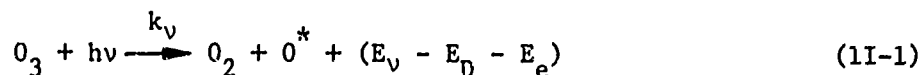
Such a scheme is capable of providing quantum yields greater than two. Large quantum yields (as high as six) have been reported for dry ozone^{4,45,46}. On the other hand, quantum yields of less than two are also reported, suggesting that any usable kinetic scheme must also include such steps as



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The following scheme contains chemical kinetic steps that are capable of representing the range of quantum yields observed, as well as the low ozone concentration thermal decomposition data. This is a requirement of an acceptable scheme.



In the following section, examination of this scheme is made with regard to quantum yields for ozone.

B. QUANTUM YIELDS FOR OZONE

The kinetic scheme given by equations (1) - (7) provides the following features:

- (a) Thermal initiation as well as photochemical initiation.
- (b) Collisional deactivation of O_2^* (a radiative lifetime greater than 10^{-9} sec is not important at high pressures).
- (c) The possibility that quantum yields of more than 2 exist for high purity ozone.
- (d) The possibility that quantum yields of less than 2 exist for low concentration ozone (in O_2).
- (e) The possibility that quantum yields are higher at high temperatures.

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- (f) The possibility that quantum yields are pressure-dependent.
- (g) The possibility that quantum yields are not independent of the radiative flux density employed in their experimental determination.

Based on the experimental work^{4,45,46} on ozone quantum yields, the aforementioned features appear to be necessary to a correct representation. Examination of the photochemical steady-state yields

$$-\frac{d}{dt} [O_3]_{ss} = 2[O_3] \left[k_1[M] + k_v \left\{ \frac{k_3 (k_4[O_3] + k_5[M])}{k_3 k_5[M] + k_6[M][O_2] \left(k_4 + k_5 \frac{[M]}{[O_3]} \right)} \right\} \right] \quad (II-8)$$

where

$$[O]_{ss} = \frac{k_1[M]}{k_2} \quad (II-9)$$

$$[O^*]_{ss} = k_v \left\{ \frac{k_4 + k_5 \left(\frac{[M]}{[O_3]} \right)}{k_3 k_5[M] + k_6 k_4 [O_2][M] + k_6 k_5 \left[\frac{[M]^2 [O_2]}{[O_3]} \right]} \right\} \quad (II-10)$$

$$[O_2^*]_{ss} = k_v \left\{ \frac{k_3 [O_3]}{k_3 k_5[M] + k_6[M][O_2] \left(k_4 + k_5 \frac{[M]}{[O_3]} \right)} \right\} \quad (II-11)$$

The quantum yield is then given by:

$$\phi \equiv \frac{-\left[\frac{d}{dt} [O_3] \right]_{ss}}{k_v [O_3]} = \left\{ \frac{2 k_1[M]}{k_v} + 2 \left[\frac{k_3 (k_4[O_3] + k_5[M])}{k_3 k_5[M] + k_6[M][O_2] \left(k_4 + k_5 \frac{[M]}{[O_3]} \right)} \right] \right\} \quad (II-12)$$

Examination of Eq. (II-12) shows that

- (a) ϕ decreases with increasing flux density due to the thermal initiation step and the fact that k_v is proportional to the

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radiative flux density (photons/cm²/sec). In the limit, where $k_v \gg k_1[M]$, ϕ becomes insensitive to k_v . In the other limit, $k_v \ll k_1[M]$, the experimental determination of ϕ is of questionable value.

- (b) For high purity ozone, $[O_3] \gg [O_2]$ and

$$\phi \longrightarrow \left[\frac{2 k_1 [O_3]}{k_v} + 2 \left\{ 1 + \left(\frac{k_4}{k_5} \right) \right\} \right] > 2$$

- (c) For low concentration ozone, $[O_3] \ll [O_2]$ and ϕ can be less than 2. (For very low concentration ozone, the back reaction associated with Eq. (2) should be included.)
- (d) For high purity ozone ϕ increases with increasing temperature. This stems from the fact that (k_4/k_5) increases with increasing temperature.
- (e) For high purity ozone, the temperature dependence of k_4 , as well as the ratio (k_4/k_5) can be determined from the quantum yield.

In order to employ this kinetic scheme, the k 's must be known. For a given case, k_v is determined from known optical extinction coefficients^{51,66} and the radiative flux density employed. Values for k_1 , k_2 , k_3 and k_4 may be selected from those reported in references 4, 55, 57, 63, and 64. k_5 and k_6 may be deduced from quantum yield data. In particular, k_5 may be deduced directly from quantum yield data for high concentration, high purity ozone (once k_4 is known). k_6 is then deduced for an intermediate case (e.g., $\phi \sim 1$).

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APPENDIX III

CLASSICAL ANALYSES OF THE STABILITY OF THE PHOTOCHEMICAL STEADY STATE

If a sample of an unstable compound is kept at a bath temperature below that required for explosion, it is taken to be in a quasi-steady state. If the sample is then subjected to a thermally and photochemically significant steady-state radiative field, the sample will then reach a new steady state (photochemical steady state) or explode. In general, the steady-state radiative flux density necessary to cause such explosions is small compared to the pulsed radiative flux densities employed in typical flash photolysis experiments. In this section, sample calculations are made using thermal theory analyses (generally acceptable at high pressures) of the ordinary and photochemical steady states.

A. MIXED HYDRAZINE FAMILY OF REACTANTS

For a cylindrical sample of N_2H_4 gas at a pressure of 46 atmospheres, a bath temperature of $T_{bc} = 502.5^\circ K$ implies an average N_2H_4 temperature of $T_{12} = 524.1^\circ K$. These are the critical conditions for explosion in the absence of a photodissociative radiative field. If the sample size is made smaller, the critical temperatures (T_{bc} and T_{12}) required for explosion increase. A plot of the steady state hydrazine sample temperatures is given in Fig. III-1, for three different sample sizes. The steady state temperature, $T_1 = T_{SS}$, corresponds to a stable sample where (dT_{SS}/dT_b) is positive and finite. Critical explosion conditions correspond to (dT_{SS}/dT_b) infinite ($T_{12} = T_{SS}$). The sample temperatures for which (dT_{SS}/dT_b) is less than zero are all unstable ($T_{SS} = T_2$). The data of Fig. III-1 are for zero radiative field.

The following table gives the variation of the photochemical steady state properties corresponding to the same sample of hydrazine under u.v. irradiation. It is seen that very low radiative flux densities ($\sim 10^{-2}$ watts/cm²) are adequate to assure sizeable $[NH_2]$ concentrations.

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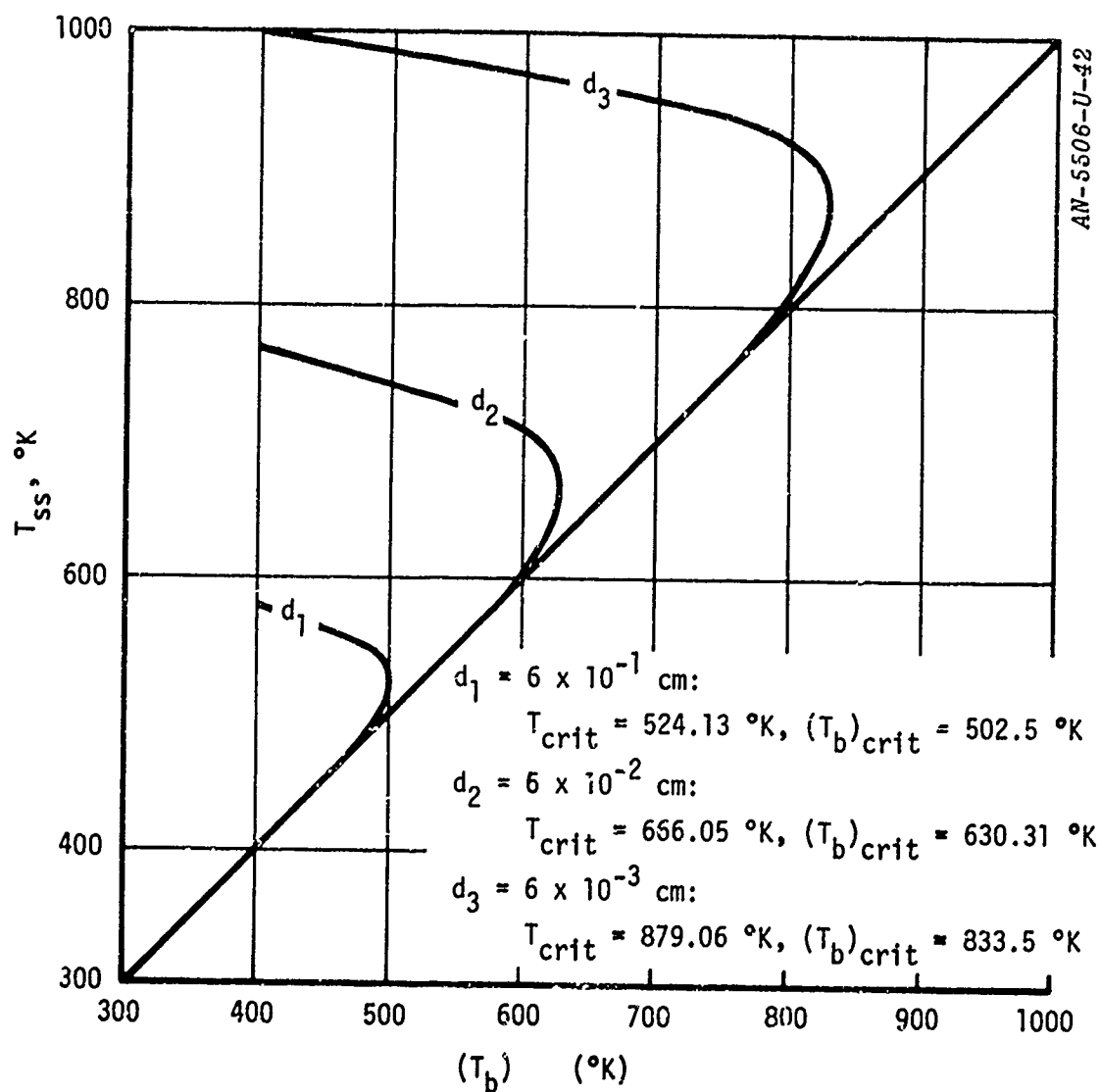


Figure III-1. Steady-State Reactant (AVG) Temperatures for 100% $[N_2H_4]$ at $P = 46$ ATM for Various (cylindrical) diameters and Bath Temperatures.

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STEADY-STATE PROPERTIES FOR N_2H_4

T_b °K	T_1 °K	T_2 °K	FLUX DENSITY Watts/cm ²	$[NH_2]_1$ moles/cm ³	$[NH_2]_2$ moles/cm ³
400	400.01	573.90	0	9.4967×10^{-15}	8.6752×10^{-12}
	490.18	547.95	7.8125×10^{-3}	6.5692×10^{-12}	6.9417×10^{-12}
	506.12	538.81	8.7891×10^{-3}	6.4290×10^{-12}	6.6519×10^{-12}
	522.39	525.83	9.2773×10^{-3}	6.4153×10^{-12}	6.4399×10^{-12}
	$T_{12} = 524.1$		9.301×10^{-3}	6.4350×10^{-12}	
450	499.90	542.70	3.906×10^{-3}	3.4507×10^{-12}	5.0180×10^{-12}
	509.37	536.57	4.395×10^{-3}	3.7576×10^{-12}	4.7263×10^{-12}
	516.49	531.09	4.639×10^{-3}	3.9833×10^{-12}	4.4970×10^{-12}
	519.42	528.56	4.700×10^{-3}	4.0789×10^{-12}	4.3995×10^{-12}
	$T_{12} = 524.1$		4.730×10^{-3}	4.2342×10^{-12}	
450	450.4	562.7	0	1.1770×10^{-13}	6.3492×10^{-12}
460	460.8	559.6		1.8477×10^{-13}	5.8108×10^{-12}
470	471.5	555.9		2.8783×10^{-13}	5.2209×10^{-12}
480	482.9	551.4		4.5168×10^{-13}	4.5747×10^{-12}
490	495.6	545.2		7.2820×10^{-13}	3.7997×10^{-12}
500	513.3	533.7		1.3621×10^{-12}	2.6624×10^{-12}
501.25	517.273	539.436		1.5584×10^{-12}	2.4000×10^{-12}
501.88	520.413	527.673		1.7309×10^{-12}	2.1959×10^{-12}
502.5		$524.1 = T_{12}$	0	1.9586×10^{-12}	

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Interestingly enough, $T_{12} = 524.1^\circ\text{K}$ is again the critical sample temperature for explosion. For a given bath temperature the critical $[\text{NH}_2]$ concentration is specified by the critical radiative flux density.

For the case of Monomethylhydrazine gas at 46 atmospheres, thermal stability calculations yield the following results:

d	T_{bc}	T_{12}
cm	$^\circ\text{K}$	$^\circ\text{K}$
0.006	666	717
0.060	493	520
0.600	394	411

For the case of unsymmetrical dimethylhydrazine gas at 46 atmospheres, thermal stability calculations yield the following results:

d	T_{bc}	T_{12}
cm	$^\circ\text{K}$	$^\circ\text{K}$
0.006	583	629
0.060	433	457
0.600	346	361

B. OZONE

As illustrated for the mixed hydrazine family of reactants, thermal stability analyses of ozone, with and without radiative fields, have been performed. Results for gaseous ozone at a pressure of 1 atmosphere are given in the following table. It is seen that rather small radiative flux densities have large effects on T_{bc} as well as the photochemical

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d cm	$(k_v)_{crit}$ sec ⁻¹	$(T_b)_c$ °K	T_{12} °K	$\{O\}$ moles/cm ³	$\{n^*\}$ moles/cm ³	$\{O_2^*\}$ moles/cm ³
0.006	2.11×10^1	200.0	293	2.97×10^{-16}	7.3×10^{-11}	2.11×10^{-8}
	1.57×10^1	225.0	304	8.9×10^{-16}	5.6×10^{-11}	1.57×10^{-8}
	1.11×10^1	250.0	318	3.3×10^{-15}	4.2×10^{-11}	1.1×10^{-8}
	7.5×10^0	275.0	335	1.5×10^{-14}	3.2×10^{-11}	7.5×10^{-9}
	4.9×10^0	300.0	359	7.8×10^{-14}	2.5×10^{-11}	4.9×10^{-9}
	3.2×10^0	325.0	384	4.4×10^{-13}	2.1×10^{-11}	3.2×10^{-9}
	2.1×10^0	350.0	413	2.3×10^{-12}	1.8×10^{-11}	2.1×10^{-9}
0.006	zero	497.19	519.7	2.2×10^{-10}	zero	zero
0.06	2.11×10^{-1}	200.0	293	2.84×10^{-16}	7.3×10^{-13}	2.1×10^{-10}
	1.57×10^{-1}	225.0	304	8.15×10^{-16}	5.5×10^{-13}	1.57×10^{-10}
	1.11×10^{-1}	250.0	317	3.0×10^{-15}	4.2×10^{-13}	1.1×10^{-10}
	7.50×10^{-2}	275.0	335	1.4×10^{-14}	3.2×10^{-13}	7.5×10^{-11}
	4.89×10^{-2}	300.0	357	7.6×10^{-14}	2.5×10^{-13}	4.89×10^{-11}
	3.5×10^{-2}	325.0	381	3.6×10^{-13}	2.0×10^{-13}	3.15×10^{-11}
	1.97×10^{-2}	350.0	402	1.2×10^{-12}	1.5×10^{-13}	1.97×10^{-11}
0.06	zero	412.2	427.3	5.2×10^{-12}	zero	zero
0.6	2.15×10^{-3}	200.0	292	1.9×10^{-16}	7.28×10^{-15}	2.15×10^{-12}
	1.57×10^{-3}	225.0	303	5.4×10^{-16}	5.5×10^{-15}	1.6×10^{-12}
	1.11×10^{-3}	250.0	317	1.9×10^{-15}	4.0×10^{-15}	1.1×10^{-12}
	7.47×10^{-4}	275.0	333	1.1×10^{-14}	3.1×10^{-15}	7.4×10^{-13}
	4.54×10^{-4}	300.0	347	2.3×10^{-14}	2.1×10^{-15}	4.5×10^{-13}
	2.10×10^{-4}	325.0	356	4.9×10^{-14}	1.1×10^{-15}	2.2×10^{-13}
	1.47×10^{-3}	350.0	362	7.9×10^{-14}	5.0×10^{-17}	1.5×10^{-14}
0.6	zero	352.9	365.6	1.3×10^{-13}	zero	zero

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steady-state concentrations of $[O]$, $[O^*]$, and $[O_2^*]$. As the sample size and bath temperature are decreased, the photochemical contribution to the explosion requirement becomes increasingly more important.

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APPENDIX IV

EXPERIMENTAL STUDIES PERFORMED ON EXPLOSIONS OF HYDRAZINE AND OF OZONE

The purpose of the experimental program was to demonstrate, for a few selected cases, the relative roles played by radiative fields in explosion. In support of the DRC program, these experiments were carried out by Rocketdyne (A Division of North American Aviation, Inc.) at their Canoga Park, California facility. Before presenting the text of the Rocketdyne report on the experimental findings, the significance of these findings will be noted.

The two systems studied experimentally are hydrazine and ozone. The salient conclusions to be drawn are:

1. It is far easier to flash initiate an explosion in ozone than in hydrazine. This experimental finding corresponds to the results of our theoretical investigation.
2. Hydrazine becomes thermally unstable just below 300°C and can decompose rapidly even where a sharp temperature or pressure pulse does not occur. From the point of view of explosion theory, such thermal instability is interpreted as an "explosion." Time-dependent examination of this thermal instability is necessary if the pressure-time and/or temperature-time history of the sample is to be described. Thus, the time-dependent theoretical studies performed at DRC correspond closely to the experimental findings: Hydrazine may become thermally unstable (with or without radiative sources) and can decompose to products without a "sharp explosion." We may arbitrarily consider a "sharp explosion" to be characterized by a reactant half-life that differs by no more than some 5 microseconds from the reactant's three-quarter life.

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3. Ozone behaves, explosively, in a more conventional manner than does hydrazine. The experimental results indicate that ozone is largely unreacted until an explosion limit is attained. A flash-initiated explosion occurs rapidly (unlike the case of hydrazine).

The unmodified text of the Rocketdyne final report to DRC on the experimental work follows:

INTRODUCTION

Experimental studies have been conducted with the objective of determining conditions for photo-initiation of explosions in certain mono-propellant compounds. Since the Rocketdyne study represents only a portion of the investigation being conducted by the Defense Research Corporation, this report will be mainly factual with the theoretical interpretation of the observed results appearing later in the formal report for the entire program.

EXPERIMENTAL

The major components of the flash apparatus were obtained from Amglo Corporation, Chicago. The flash lamps used had a linear tubular quartz envelope, a one inch arc length, and were filled with argon and mercury for best ultraviolet output. A bank of ten 50-microfarad condensers was used for energy storage and a 0-5000 volt power supply was used for charging the condensers. At voltages below the breakdown voltage of the lamps (800 volts for lamps mentioned above), a trigger supply which provides a very high voltage pulse was used to initiate the flash. At voltages above the self-flash voltage of the lamp, a special relay was used to switch the condenser voltage to the lamp, which then flashed without further triggering. For most of the work reported the lamps were used at their maximum rating of 500 J of electrical energy, which corresponds to 500 microfarads at 1400 volts.

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An inductance of 600 μ H was used in series with the lamp to reduce the peak current and thus increase lamp lifetime. From information provided by the supplier, flash duration for the system used is of the order of 400 microseconds (to 1/2 maximum intensity) with the inductance in the circuit, and 200 microseconds without the added inductance.

Lamp output may be estimated from published data. Porter reports 10^{20} quanta in the 2000-4000Å interval from a 1000 J flash of an Xe filled lamp (Ref. 1). Commercial lamps are reported to have efficiencies of 10-50 lm/W.s (Ref. 2), presumably in the wavelength region of approximately 3500-7500Å. Strong (Ref. 3) reports that their Xe-filled quartz lamps produce a continuum plus Xe lines with intensity roughly independent of wavelength down to 3000Å (decreasing somewhat between 4600 and 5600Å to a minimum at 5100Å of about 60% of the average intensity). The wavelength region covered was 2400-6500Å. Using these values, it is estimated that flash lamps used in the present study produce a total of approximately 15 J of energy as light in each 1000Å interval for a 1000 J (electrical energy discharged) flash over the wavelength region of 2000 to 8000Å.

With a lamp to cell distance of about one inch, the amount of light reaching the sample is estimated to be about 1% of that emitted by the flash, because of geometric factors, scattering by the quartz sample tube, etc. This estimate assumes a 6-mm ID sample tube one-inch long with a reflector behind the lamp.

The sample tubes employed were constructed from 1 mm ID fused silica capillary and 3 mm and 6 mm ID fused silica tubing. By sealing water in the tubes and heating slowly until the tube ruptured, it was established that the 1 mm capillary could contain pressure in excess of 3000 psi; the 3 mm tubing ruptured at about 1000 psi and the 6 mm about 400 psi. The hydrazine samples were sealed in sample tubes by freezing the hydrazine, evacuating the system, and torching the sample tube shut. The ozone sample tubes were filled through a stopcock.

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Heaters were constructed of aluminum rod drilled to contain the sample tube and a thermocouple and wrapped with resistance wire and asbestos. A remote control device was constructed to insert the sample tube into the heater and withdraw it to a position next to the flash lamp. The apparatus was surrounded by heavy shielding for safety. It was found that on insertion of the sample tube into the heater, the sample reached essentially the heater temperature in two minutes. This method of operation was chosen to reduce the time the sample was heated prior to exposure to the flash.

Ozone was prepared from cylinder oxygen in a Pyrex apparatus (Ref. 4) consisting of two tubes sealed with an annular space about 3 mm across, where the oxygen was subjected to an electric discharge from a 10,000 volt ignition transformer. The ozone ex was operated in an ice bath at 0 C to improve yields. The gas mixture was analyzed for ozone by bubbling it through a neutral buffered KI solution and titrating the I_2 produced ($O_3 + 2H^+ + 2I^- \rightarrow O_2 + H_2O + I_2$) with thiosulfate (Ref. 5). It was found that the ozone yield at atmospheric pressure varied from 5.3 w/o with an oxygen flow rate of 130 cc/min to 1 w/o at a flow rate of 830 cc/min. The ozone was handled in a vacuum system with stopcocks lubricated with Halocarbon grease (Halocarbon Products Co.). In operation, a 170 cc volume was flushed out and filled at atmospheric pressure with approximately 5% ozone in oxygen. Then liquid nitrogen was placed on the attached sample tube (volume about 8 cc) and most of the ozone and oxygen frozen out. With the sample tube in liquid nitrogen the oxygen was pumped off, leaving a droplet of nearly pure ozone, which was easily visible to the eye. The stopcock was then closed and the ozone allowed to vaporize in the 8 cc sample tube. For higher temperature operation the sample tube was heated with hot air blown over it and the temperature was read from a thermocouple in a similar tube next to the sample tube. Again the sample apparatus was enclosed in shielding, and heating, operation of liquid nitrogen dewar, etc. were carried out remotely. A two-inch thick Lucite block allowed observation.

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RESULTS AND DISCUSSION

HYDRAZINE

When the hydrazine sample tubes (3 mm and 1 mm ID) initially 20% filled with liquid hydrazine were heated slowly, they ruptured violently at about 250 C. It is believed that these were pressure "explosions" caused by the slow thermal decomposition of the hydrazine. Since the critical density of hydrazine is 0.234 gm/cc, the tubes could not have been burst by hydrostatic pressure. The vapor pressure of hydrazine is about 900 psi at 290 C--below the measured bursting pressure of the sample holder tubing. However, the calculated final pressure of non-condensable gas (N_2 and possibly H_2) if slow decomposition should occur, 4500 psi at 300 C, exceeds the burst pressure of the tubing.

One mm tubing initially about 5% filled with liquid hydrazine did not rupture after heating at 300 C for several hours. At the conclusion of the heating, liquid was visible in the tube (at room temperature) in quantity slightly less than initially present. This liquid vaporized immediately at room temperature when the tube was opened, leading to the conclusion that most of the hydrazine had decomposed to form ammonia, since hydrazine vaporizes slowly under these conditions. The calculated final pressure in this case, 1100 psi, is less than the 3000 psi necessary to burst the capillary tubing.

A variety of samples of hydrazine were flashed, but since no explosions occurred, only the most severe conditions will be mentioned. In one experiment with hydrazine, an apparent explosion did occur but subsequent investigation revealed that the flash lamp probably exploded taking the sample cell with it. The inductance was placed in the circuit in the remainder of the experiments to greatly reduce the probability of a lamp failure of this type.

Liquid hydrazine was flashed at room temperature in a 3 mm tube with no explosion. 6 mm tubes with volume about 1 cc and containing

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0.05 gm hydrazine were placed in the 315°C heater for 2 minutes and then flashed with no explosion. These tubes later ruptured while being heated further to 340-360 C. The results indicate than an explosion did not occur and would have been detected had it occurred.

It is concluded that initiation of an explosion in hydrazine with light is relatively difficult, even at temperatures at which thermal decomposition is occurring rather rapidly. Because of this thermal decomposition, attempts at higher temperatures are not feasible unless a very fast heating technique could be developed. Since it appears that hydrazine must be heated near its thermal decomposition temperature before photoinitiated explosions can be observed, it is recommended that in future studies the experiment be designed so that the concentration of the hydrazine can be monitored continuously up to the time the flash is triggered. The inclusion of a pressure transducer in the system would also be quite useful.

OZONE

Calculations based on the oxygen vapor pressure and cell volumes predict an ozone pressure of 600 mm in the sample tube at room temperature. This was doubled in some cases by filling the measuring volume twice. No difficulty was experienced in producing or handling the ozone. It was stable for 24 hours in the apparatus at room temperature as evidenced by visual observation of readily condensible ozone after that time. The ozone was heated to 70°C for a period of about a minute and was again observed visually on freezing down; therefore, thermal decomposition was not a problem under the conditions employed in this investigation. Available rate constants substantiate this conclusion (Ref. 4).

With a lamp positioned about 4.5 cm from a 6 mm sample tube (no reflector), ozone was still observed in about the same amount on freezing down after flashing at room temperature when either 600 or 1200 mm of ozone were employed. With a lamp positioned 2 cm from the sample tube

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and with an aluminum foil reflector 1/2 inch behind the lamp, no ozone was visible on freezing down after one flash (500 J) at either 25 or 70°C and with 600 or 1200 mm pressure. The tube did not rupture, presumably because of the relatively low pressure of gas (even if the conditions of the decomposition approached adiabatic). Because of the apparent disappearance of all of the ozone, it may be assumed that a very rapid reaction (explosion) occurred. McGrath and Norrish (Ref. 6) have shown that the decay of ozone after a flash is very rapid, and the presumption of an explosion on the evidence of substantially complete destruction of ozone seems to be valid.

An attempt was made to explode condensed ozone by flashing immediately upon removal of the liquid nitrogen bath, before the ozone evaporated. There was no apparent effect of the light.

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REFERENCES FOR APPENDIX IV

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2. G. E. Flashtube Data Manual, General Electric Co., Photo Lamp Dept.
3. R. L. Strong, et al., J. Chem. Phys. 26 1287 (1957).
4. A. E. Axworthy, Ph.D., Dissertation, Univ. of Southern California, 1959 (University Microfilm, Ann Arbor, Michigan-L.C. Card no. M.C. 59-1837).
5. D. H. Byers and B. E. Saltzman, p. 93 in Ozone Chemistry and Technology Advances in Chemistry Series #21 (1959).
6. W. D. McGrath and R.G.W. Norrish, Proc. Royal Soc. (London) A242 265 (1957).

This concludes the unmodified text of the Rocketdyne final report to DRC on the experimental work.

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APPENDIX V THE COMPUTER PROGRAM

A computer program (HYDRA) was written in FORTRAN for the Control Data Corporation 3600 computer to perform three types of calculations at the option of the user. The main function involved the integration of Eqs. (16)-(20) of Section VI to describe the time dependent behavior of the system. For this a fourth-order Runge-Kutta integration with variable integration interval was used. The remaining two options allow the user to iterate on the bath temperature or initial radiation flux to determine the critical value, i.e., that which makes R and L tangent (see Section V).

The input consists of 50 cards for the first case after which one or more parameters may be varied for subsequent cases by adding the appropriate cards. Specifically, the input is as follows:

Card 1) Fortran format 3E20.10, 2I5

DX: Initial integration interval
AE: Absolute allowable error for integration interval control
RE: Relative allowable error for integration interval control
IFVD: $\begin{cases} 0 & \text{variable interval control} \\ 1 & \text{fixed interval is used for integration} \end{cases}$
NMAX: maximum number of integration steps allowed

Card 2) Reactant identifier card

Cols. 13-39 identifier of fuel F (e.g., N_2H_4)
Cols. 23-29 identifier of reactant A (e.g., NH)
Cols. 33-39 identifier of reactant B (e.g., N_2H_3)
Cols. 43-49 identifier of reactant C (e.g., N_2H_4)

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Cards 3-49) Parameter List

Cols. 1, 2 code identifying parameter

Cols. 13-19 name of parameter

Cols. 21-40 value of parameter in E20.11 format

Cols. 55-70 units which parameter is given in

According to the following list:

<u>Code</u>	<u>Parameter</u>	<u>Code</u>	<u>Parameter</u>	<u>Code</u>	<u>Parameter</u>	<u>Code</u>	<u>Parameter</u>
01	P_o	14	h_6	27	P_o	40	$C_{k_{vB}}$
02	T_b	15	h_7	28	P_1	41	C_i
03	F_o	16	C_{k_1}	29	S_{P_1}	42	t_o
04	ρ	17	E_{k_1}	30	dS_{P_1}	43	T_o
05	C_p	18	C_{k_2}	31	P_2	44	F_o
06	ϵ	19	E_{k_2}	32	S_{P_2}	45	A_o
07	λ	20	C_{k_5}	33	dS_{P_2}	46	B_o
08	d	21	E_{k_5}	34	ΔT_b	47	C_o
09	Δ_E	22	C_{k_6}	35	dT_b	99	end
10	Δ_H	23	E_{k_6}	36	ΔP_o		
11	h_I	24	C_{k_7}	37	dP_o		
12	h_2	25	E_{k_7}	38	t_{max}		
13	h_5	26	$C_{k_{vT}}$	39	C_{df}		

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The first parameter gives the pressure which is not used in the calculations and is included for reference only. Parameters 2-5, 7, 8, 10-15 are as in Section VI. Parameter 6 and 26-33 are used to give the time dependent k_v according to the formula

$$k_v = C_{k_v} \text{ (moles/watt-sec)} \times \epsilon \text{ (cm}^2\text{/mole)} \times P \text{ (watts/cm}^2\text{)}$$

$$P = \begin{cases} P_0 \text{ watts/cm}^2 & 0 \leq t \leq S_{P_1} - dS_{P_1}/2 \\ P_1 \text{ watts/cm}^2 & S_{P_1} + dS_{P_1}/2 \leq t \leq S_{P_2} - dS_{P_2}/2 \\ P_2 \text{ watts/cm}^2 & S_{P_2} + dS_{P_2}/2 \leq t \end{cases}$$

In the transition regions, $S_{P_1} - dS_{P_1}/2 \leq t \leq S_{P_1} + dS_{P_1}/2$;

$S_{P_2} - dS_{P_2}/2 \leq t \leq S_{P_2} + dS_{P_2}/2$, the value of P changes smoothly from one value to the next using a fifth order polynomial having zero first and second derivatives at the end points. The value of $C_{k_{vT}}$ (parameter 26) is used to compute k_v in dT/dt while $C_{k_{vB}}$ (parameter 40) is used to compute k_v as it enters into dB/dt . This allows the user to distribute the effect of the radiation into thermal energy or dissociation in any ratio he chooses.

Parameters 16-25 are used to compute the rate constants according to the formula

$$k_i = C_{k_i} e^{-E_{ki}/R} \quad (E_{ki} = E_i/R)$$

Parameters 34 and 35 are used in the iterations of T_b to determine the critical value. One must input a value of T_b as a negative number, for which the R and L curves intersect. Then the program starts increasing T_b by the amount ΔT_b until this condition is violated. It then proceeds to converge on the critical value until consecutive values of T_b are within the range $\pm \Delta T_b$.

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Parameters ΔP_0 and dP_0 perform the same function for the k_{v0} iterations and the same rules apply.

In some cases, the user may want the time dependent behavior of the system under conditions where the fuel concentration remains constant. Parameter 39 performs this function as it multiplies the expression for dF/dt in the program. Thus it should have the value 1 for normal operation, 0 when the fuel concentration is to remain constant.

Parameter 38 acts as a control on computer time. It represents the maximum value of t to which integration can proceed.

Normally, the initial conditions on the dependent variables (with the exception of F_0) are taken as the steady state values. Parameter 41 overrides this if it is input as any non-zero quantity. In that case the initial conditions are taken from parameters 42-47.

The last card merely indicates to the program that it has completed reading data for a particular case.

The user has the option of using his own identification for the above parameters (1-47); however, some identification should be entered as the program writes this same information as output to identify the case.

If one wishes to run additional cases, only those parameters which change need additional input cards followed by a "99" card.

Some additional remarks on the data contained in the first card should be made. The integration subroutine used in the program controls the integration interval size by comparison of Runge-Kutta integration over two half-intervals with a Simpson's rule sum of the resulting values. Thus if ΔI_{SR} is the incremental change in the dependent variable according

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to Simpson's rule and ΔI_{RK} is the same as determined by Runge-Kutta, the criterion for increasing or decreasing the interval is determined by the term

$$\frac{\Delta I_{RK}}{A} + \frac{-\Delta I_{SR}}{RI}$$

where I is the current value of the dependent variable and A and R are the absolute and relative allowable errors given on the first card.

The program listing follows with the exception of the RKS3 numerical integration subroutine. This is a standard subroutine available, for example, through the IBM Share Library.

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PAGE 1 OF PROGRAM HYDRA

PAGE 1

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PROGRAM HYDRA
COMMON Z,LABEL,DATA,NAME,ZS,US,TS,DRS,XLS,C1,C2,C3,C4,
+                                     C5,C6,C7,
X RS,C8,TEST1,TEST2,DIV,UL,DUL,USTART,UCR1,UCR2,TCR1,
+                                     TCR2,RPR,XLPR,
X F,E1,T1,T2
COMMON/I/ IK1,IK2,IK5,IK6,IK7,IPUMP,NCOUNT,NMAX
COMMON/DE/
+U,DU,S,DS,WORK,AE,RE,T3,T4,T5,T6,T7,T8,T9,VP,SS,SCH1,
X SCH2,SCH3,SCH4,A1,A2,P,T,DE1,DK1,DE2,DK2,DE5,DK5,DE6,
+                                     DK6,DE7,DK7,
X TPU,C9,C10,STOP,FSTOP
DIMENSION
+ Z(100),LABEL(100),DATA(8),NAME(4),ZS(2),TS(2),US(2),
X RS(2),DRS(2),XLS(2),UNITS(100,2)
DIMENSION U(5),DU(5),AE(5),RE(5),WORK(50),VP(51,13)
EXTERNAL PHD,PHC

C                                     INTEGRATION
+                                     PARAMETERS ON THE
C                                     FIRST CARD
C
1000 READ (60,1010) DS,AU,RO,IFVD,NMAX
1010 FORMAT(3E20,11,2(5)
DO 1011 I=1,100
1011 Z(I) = 0.0

C                                     READ REACTANT NAMES
+                                     AND INPUT
C                                     PARAMETERS
C
1020 IIT = 1
1020 READ(60,1030) INP,DATA
1030 FORMAT(12,8X,7A8,A6)
1040 IF(EOF,60) 1041,1050
1041 CALL EXIT
1050 IF(INP,EQ,99) GO TO 1121
1060 IF(INP,NE,0) GO TO 1100
1070 DECODE(64,1080,DATA) NAME
1080 FORMAT(4(2X,R8))
1090 GO TO 1020
1100 DECODE(64,1110,DATA)
+                                     LABEL(INP),Z(INP),(UNITS(INP,J),J=1,2)
1110 FORMAT(2X,A8,10X,E20,11,4X,2A8)

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CCC

TEST FOR STABILITY

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PAGE 4 OF PROGRAM HYDRA

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1590 DIV = 2.0
1600 UL = UL-DUL/DIV
1610 IF(DUL,LE,1.0E-08) GO TO 1640
1620 DUL = DUL/DIV
1630 GO TO 1540
1640 JSTART = UL
1650 TEST2 = R(1L)+C8*UL
1660 IF(TEST2)1/20,1700,1670
1670 GO TO (1673,1671,1671) IIT
1671 WRITE(61,1482) Z(2),Z(27)
1673 WRITE(61,1680) UL,TL,TEST2,TEST1
1680 FORMAT(/// 71H IMPOSSIBLE TO MEET STABILITY
      +
      + CRITERION. MINIMUM OF
      X R-L OCCURS AT U = E20,11,10X, 5H T = E20,11,// 30H
      + WHERE IT HAS
      X THE VALUE R-L = E20,11,10X,10H D(R-L) = E20,11)
1690 GO TO (1020,2490,2600) IIT
1700 TCR1 = TCR2 = TL
1701 UCR1 = UCR2 = UL
1710 GO TO 2020
1720 DIV = 1.0
1730 DUL = 0.1*UL
1740 GO TO 1780
1750 TL = UL+Z(2)
1760 TEST2 = R(1L) -C8*UL
1761 IF((TEST2,LE,0.0),AND,(ABSF(UL),LE,1.0E-08))GO TO 1850
1770 IF(TEST2)1780,1850,1800
1771 UCR1 = UL
1780 JL = MAX1F(0.0,UL-DUL/DIV)
1790 GO TO 1820
1800 DIV = 2.0
1801 JCR1 = UL
1810 UL = UL+DUL/DIV
1820 IF(DUL,LE,1.0E-08) GO TO 1860
1830 DUL = DUL/DIV
1840 GO TO 1750
1850 UCR1 = UL
1860 TCR1 = UCR1 +Z(2)
1870 DUL = 0.1*(USTART)
1880 UL = USTART + DUL
1890 DIV = 1.0
1900 TL = UL + Z(2)

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PAGE 5 OF PROGRAM HYDRA

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1910 TEST2 = R(TL) - C8*UL
1911 IF((TEST2,LE,0.0),AND,(TL,GT,STOP)) GO TO 2000
1920 IF(TEST2)1930,2000,1960
1930 UCR2 = UL
1940 UL = UL + DUL/DIV
1950 GO TO 1990
1960 DIV = 2.0
1970 UCR2 = UL
1980 UL = UL-DUL/DIV
1990 IF(DUL,LE,1.0E-08) GO TO 2010
1991 DUL = DUL/DIV
1992 GO TO 1900
2000 UCR2 = UL
2010 TCR2 = UCR2 +Z(2)
2020 UL = UCR1
2030 DUL = (UCR2-UCR1)/40.0
2040 IF(DUL,EQ,0.0) GO TO 2132
      GO TO (2041,2043,2043) IIT
2041 WRITE(61,2042)
2042 FORMAT(1H1,53H THE FUNCTIONS R AND L BETWEEN POINTS
      + OF INTERSECTION
      XN // 14X,1HU,24X,1HT,24X,1HR,24X,1HL,20X,4H R=L //)
      GO TO 2050
2043 WRITE(61,2044) Z(2),Z(27)
2044 FORMAT(1H1,67H THE FUNCTIONS R AND L BETWEEN THE
      + POINTS OF INTERSE
      XCTION FOR IB = E20,11,10X,5HP0 = E20,11,//
      + 14X,1HU,24X,1HT,24X,1HR
      X,24X,1HL,20X,4H R=L //)
2050 DO 2130 I=1,41
2060 TL = UL +Z(2)
2070 RPH = R(TL)
2080 XLPR = C8*UL
2090 TEST2 = RPH -XLPR
2100 WRITE(61,2110) UL,TL,RPH,XLPR,TEST2
2110 FORMAT( 5(4X,E20,11))
2120 UL = UL +DUL
2130 CONTINUE
2131 GO TO 2140
2132 WRITE(61,2133) UCR1
2133 FORMAT(/// 32H R AND L ARE EQUAL ONLY AT U = E20,11)
C

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PAGE 6 OF PROGRAM HYDRA

PAGE 6

C
C

FIND TS AND TSP

```

2140 ZS(1) = 0.0
2150 ZS(2) = Z(26)
2160 DO 2380 K=1,2
2170 DIV = 1.0
2180 UL = 0.0
2190 DUL = 5.0
2200 Z(26) = ZS(K)
2210 TL = UL + Z(2)
2220 F = C8*UL - R(TL)
2230 IF(F)2240,2380,2270
2240 US(K) = UL
2250 UL = UL + DUL/DIV
2260 GO TO 2300
2270 DIV = 2.0
2280 US(K) = UL
2290 UL = UL-DUL/DIV
2300 IF(DUL,LE,1.0E-08) GO TO 2330
2310 DUL = DUL/DIV
2320 GO TO 2210
2330 US(K) = UL
2340 TS(K) = US(K) +Z(2)
2350 RS(K) = H(TS(K))
2360 DRS(K) = DR(TS(K))
2370 XLS(K) = C8*UL
2380 CONTINUE
2390 WRITE(61,2400)
      + US(1),US(2),TS(1),TS(2),RS(1),RS(2),XLS(1),XLS(2),
      + DRS(1),DRS(2),C8,C8
2400 FORMAT(/// 4X,51H THERMAL STEADY STATE //
      + PHOTOCHEMICAL STEADY ST
      + XATE // 1X,2H U,2X,E20,11,10X,E20,11,/ 3H
      + T,2X,E20,11,10X,E20,11,/
      + X 3H R,2X,E20,11,10X,E20,11,/ 3H
      + L,2X,E20,11,10X,E20,11,/ 3H DR,
      + X 2X,E20,11,10X,E20,11,/ 3H DL,2X,E20,11,10X,E20,11)
2480 GO TO (2701,2520,2640) IIT
2490 DIVT = 2.0
2500 THH = Z(2)
2501 Z(2) = Z(2) -DET8/DIVT
2510 GO TO 2540

```

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SET UP INITIAL CONDITIONS AND INTEGRATION PARAMETERS

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PAGE 8 OF PROGRAM HYDRA

PAGE 8

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      IF(E2.LE,-700.0) GO TO 2730
      T2 = EXPF(E2)
      GO TO 2740
2730  T2 = 0.0
2740  U(4) = Z(3)*(T1 +T2)
      U(5) = 0.0
      U(1) = US(1)
      S = 0.0
      GO TO 2743
2741  S = Z(42)
      DO 2742 J=1,5
2742  U(J) = Z(42+J)
2743  NPR = 0
      IBKP = 1
      NTRY = 1
      NE = 5
      DO 2750 I=1,NE
      AE(I) = AD
2750  RE(I) = R0
      IF(Z(30).EQ.0.0) GO TO 2760
      SCH1 = Z(29) -Z(30)/2.0
      SCH2 = Z(29) + Z(30)/2.0
      SCH3 = MAX1F(SCH2,Z(32)-Z(33)/2.0)
      SCH4 = Z(32) + Z(33)/2.0
      IF(SCH2.LT.SCH4) GO TO 2760
      Z(30) = 0.0
2760  CALL RKS3(PHD,PHC,U,DU,AE,RE,WORK,S,DS,NE,IFVD,IBKP,
               NTRY,IERR)
      IF(IERR.EQ.0) GO TO 1020
      WRITE(61,2770) IERR
2770  FORMAT(/// 17H ERROR RETURN OF 16,10H FROM RKS3 )
      CALL INTER
      GO TO 1020
      END
```

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APPENDIX VI

**PRINTOUT OF A TYPICAL COMPUER RUN
OF THE EXPLOSIVE TRAJECTORY OF AN IRRADIATED UDMH SAMPLE**

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TIME	UT	OF	HA	DM	DC	UDF
3.0886303-004	1.14580428-009	-6.95843963-002	5.934215948-002	3.26290229-007	-8.86053926-000	-1.83506323-015
3.0886303-004	1.138553338-009	-7.10621703-002	5.934215948-002	3.40153636-002	-9.41721489-000	-2.3636967-015
3.0886303-004	1.138553338-009	-7.19763205-002	5.934215948-002	3.40153636-002	-9.76912870-000	-2.3636967-015
3.0886303-004	1.12704661-009	-7.33086156-002	5.88452778-002	3.61786017-002	-1.08777534-001	-3.4662422-015
3.0886303-004	1.11420422-009	-7.47201057-002	5.84137036-002	3.74367469-002	-1.08777534-001	-3.79610362-015
3.0886303-004	1.10797583-009	-7.59258944-002	5.78053153-002	3.86144420-002	-1.14218364-001	-4.34799489-015
3.0886303-004	1.096368174-009	-7.71493213-002	5.71425544-002	3.97210994-002	-1.19542133-001	-4.8988705-015
3.0886303-004	1.08336866-009	-7.80611171-002	5.62941240-002	3.97999022-002	-1.24710663-001	-5.44513343-015
3.0886303-004	1.06901323-009	-7.89157145-002	5.53057600-002	6.13018508-002	-1.29665263-001	-5.932189-015
3.0886303-004	1.05332019-009	-7.97107059-002	5.41170525-002	6.24779359-002	-1.34427266-001	-6.58935489-015
3.0886303-004	1.03827452-009	-8.01294499-002	5.29169108-002	6.31796939-002	-1.38994603-001	-7.01974497-015
3.0886303-004	1.01807040-009	-8.07796169-002	5.15238020-002	6.37937853-002	-1.43062377-001	-7.51069583-015
3.0886303-004	9.98611216-008	-8.1110712-002	5.00019930-002	6.42808041-002	-1.46883970-001	-7.97854795-015
3.0886303-004	9.85741194-008	-8.12293292-002	4.89795568-002	6.44153908-002	-1.49104389-001	-8.26041678-015
3.0886303-004	9.72433403-008	-8.12795921-002	4.79102860-002	6.45852883-002	-1.51167878-001	-8.53882043-015
3.0886303-004	9.58703500-008	-8.12828673-002	4.67952258-002	6.46900354-002	-1.53867720-001	-8.78910180-015
3.0886303-004	9.44588364-008	-8.11789990-002	4.56393313-002	6.47374491-002	-1.57079749-001	-9.03443546-015
3.0886303-004	9.30076424-008	-8.10271767-002	4.44394858-002	6.47273187-002	-1.58351520-001	-9.26612444-015
3.0886303-004	9.15216233-008	-8.08072618-002	4.32014715-002	6.46592098-002	-1.57224814-001	-9.48362566-015
3.0886303-004	9.00222994-008	-8.05192949-002	4.19244023-002	6.45329104-002	-1.58913143-001	-9.66323535-015
3.0886303-004	8.84528662-008	-8.01532888-002	4.06117934-002	6.43843432-002	-1.59913342-001	-9.8736427-015
3.0886303-004	8.68733687-008	-7.97400484-002	3.92747643-002	6.41860221-002	-1.60721851-001	-1.08453000-016
3.0886303-004	8.52875335-008	-7.92502501-002	3.79028165-002	6.38061424-002	-1.61335772-001	-1.12807425-016
3.0886303-004	8.36407923-008	-7.86949276-002	3.65044488-002	6.34494803-002	-1.61759662-001	-1.183398416-016
3.0886303-004	8.19921193-008	-7.80751640-002	3.50791933-002	6.30367734-002	-1.61987478-001	-1.24622581-016
3.0886303-004	8.03253223-008	-7.73938842-002	3.36326160-002	6.25897242-002	-1.62021834-001	-1.35673805-016
3.0886303-004	7.86431984-008	-7.66498444-002	3.21603201-002	6.20490818-002	-1.61854206-001	-1.46565248-016
3.0886303-004	7.69482958-008	-7.56767629-002	3.06829030-002	6.14765729-002	-1.61516378-001	-1.57285676-016
3.0886303-004	7.52433433-008	-7.49885961-002	2.91849858-002	6.08539185-002	-1.60982304-001	-1.67837027-016
3.0886303-004	7.35099435-008	-7.40153435-002	2.76725015-002	6.01330112-002	-1.60266099-001	-1.78222113-016
3.0886303-004	7.18137745-008	-7.31058215-002	2.61560058-002	5.94554037-002	-1.59371937-001	-1.88443120-016
3.0886303-004	7.00943141-008	-7.20953051-002	2.46303620-002	5.87847938-002	-1.58302727-001	-1.98502349-016
3.0886303-004	6.83752797-008	-7.10344684-002	2.30983355-002	5.79020098-002	-1.57367154-001	-2.08403043-016
3.0886303-004	6.65895888-008	-6.99302643-002	2.15677643-002	5.70594986-002	-1.56700834-001	-2.18153630-016
3.0886303-004	6.49478898-008	-6.87857556-002	2.00362495-002	5.61812727-002	-1.56123053-001	-2.2753255-016
3.0886303-004	6.32441538-008	-6.76040644-002	1.85007603-002	5.52864732-002	-1.55885080-001	-2.37209110-016
3.0886303-004	6.15502238-008	-6.63884527-002	1.69840611-002	5.43242689-002	-1.55588508-001	-2.4652793-016
3.0886303-004	5.9861638-008	-6.51431019-002	1.54677822-002	5.33213813-002	-1.48619364-001	-2.55712333-016
3.0886303-004	5.82081169-008	-6.38832943-002	1.39608298-002	5.23525608-002	-1.46329684-001	-2.64772129-016
3.0886303-004	5.65477746-008	-6.25702836-002	1.24681703-002	5.13856555-002	-1.43326643-001	-2.73712812-016
3.0886303-004	5.49131198-008	-6.12513471-002	1.09826648-002	5.02881537-002	-1.42017198-001	-2.82541313-016
3.0886303-004	5.32779239-008	-5.99146875-002	0.95150852-002	4.92280687-002	-1.38611855-001	-2.91264721-016
3.0886303-004	5.1707667-008	-5.86342255-002	0.80648791-002	4.81529583-002	-1.37118994-001	-3.009903107-015
3.0886303-004	5.01326790-008	-5.72007034-002	0.66311523-002	4.70855913-002	-1.34547421-001	-3.104253936-015
3.0886303-004	4.85832575-008	-5.58295477-002	0.52173598-002	4.59664648-002	-1.31905914-001	-3.198773600-015
3.0886303-004	4.70476613-008	-5.44528715-002	0.37625399-002	4.48441331-002	-1.29203159-001	-3.29551661-015
3.0886303-004	4.55062319-008	-5.30725090-002	0.22550223-002	4.37550398-002	-1.26447855-001	-3.39561141-015
3.0886303-004	4.40062780-008	-5.16941761-002	0.11079256-002	4.26335389-002	-1.23647730-001	-3.49807303-015
3.0886303-004	4.2554724-008	-5.03174774-002	0.05464016-002	4.15310873-002	-1.20911473-001	-3.60003359-015
3.0886303-004	4.10436974-008	-4.89459576-002	0.00888250-002	4.04222303-002	-1.17846710-001	-3.70426344-015

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TIME	T	F	A	H	C	P
3.62853244-004	1.34139430-003	2.83407747-005	3.64778927-005	1.540-999-005	5.13081370-007	5.08890000-002
3.69059848-004	1.34201511-003	1.95974072-005	3.6435874-005	1.927-0035-005	4.25055869-007	5.08000000-002
3.69836433-004	1.34601511-003	1.80754311-005	3.64830713-005	9.251-1385-002	4.77588931-007	5.08000000-002
3.69836818-004	1.34319428-003	1.81745953-005	3.65451916-005	5.3152423-005	4.60423528-007	5.08000000-002
3.69859603-004	1.34375323-003	1.74947236-005	3.65974823-005	5.37149701-005	4.43798408-007	5.08000000-002

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TIME	LT	UF	UA	UB	DC	DD
3.00054200-004	3.00010403-000	-0.70017224-002	3.72145774-002	3.93166502-002	-1.12060979-001	-0.62502348-015
3.00054040-004	3.00009070-000	-0.02272110-002	3.55690240-002	3.52170122-002	-1.12161501-001	-0.43213000-015
3.00050430-000	3.71500070-000	-0.40044100-002	3.47204410-002	3.71251015-002	-1.03255166-001	-0.23671042-015
3.00050010-000	3.50021130-000	-0.35520290-002	3.35500061-002	3.60420408-002	-1.00340513-001	-0.03809720-015
3.00050000-000	3.40000120-000	-0.22414091-002	3.123063007-002	3.40715678-102	-1.03447721-001	-7.033933698-015

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THE FUNCTIONS M AND L BETWEEN POINTS OF INTERSECTION

	U	T	A	L	M-L
J	1.70819016712-002	2.50817081674-002	4.21951635240-002	4.21951635244-007	6.96942503784-014
T	1.9989560512-008	2.5199955604-002	5.54973996716-007	4.7193623674-015	-4.6638446466-905
A	3.06411028856-008	2.53964110289-002	7.20863791806-007	9.3964857503-005	-9.32372519474-085
L	5.93724489192-000	2.55937244895-002	9.47979740092-007	1.4673516712-004	-1.39787186073-003
DL	7.9364194953-000	2.5791841949-002	1.23137951543-006	1.8750623966-004	-1.86274860483-004
	9.86357489801-008	2.5988357410-002	1.59318185967-006	2.3627311174-014	-2.32664150134-004
	1.18567287023-001	2.61856728705-002	2.05022061201-006	2.81043848459-004	-2.78999133447-004
	1.30298643859-001	2.63829863304-002	2.6361953616-006	3.2619456146-004	-3.25183270761-004
	1.5084879082-001	2.65803837084-002	3.37265535249-006	3.7456526233-004	-3.71213442802-004
	1.77761925128-001	2.6778192509-002	4.29773221366-006	4.2193160317-004	-4.17063406184-004
	1.97493371164-001	2.69749347114-002	5.45822871800-006	4.80132672389-004	-4.82674451676-004
	2.1225617195-001	2.71722981728-002	6.90794977613-006	5.14903744805-004	-5.07093794782-004
	2.36994564331-001	2.7365656320-002	8.71303106844-006	5.61674616569-004	-5.52961725509-004
	2.568868927-001	2.75608818025-002	1.09534773065-005	6.0644568041-004	-5.97492413349-004
	2.76419635393-001	2.77641963539-002	1.3729217082-005	6.55215900737-004	-6.41491743066-004
	2.96151281338-001	2.79615128136-002	1.71936094559-005	7.01986032021-004	-6.8444363364-004
	3.15802747370-001	2.81580274729-002	2.13468975300-005	7.46759104905-004	-7.27412807398-004
	3.35614293456-001	2.83561429345-002	2.44995673615-005	7.95530176989-004	-7.6903050933-004
	3.55345939437-001	2.8553459394-002	3.27988656241-005	8.42630249662-004	-8.09583183444-004
	3.75877485473-001	2.87587738545-002	4.0474915027-005	8.9077523146-004	-8.48597502545-004
	3.95808931509-001	2.89480893151-002	4.92034627697-005	9.35643533238-004	-8.86037960451-004
	4.1548077539-001	2.91454807753-002	6.11150477931-005	9.82014405314-004	-9.21499417409-004
	4.34272323591-001	2.93427232362-002	7.47367426667-005	1.02938553748-003	-9.54500794008-004
	4.54083565612-001	2.95408356561-002	9.12703662940-005	1.07613660966-003	-9.84886243587-004
	4.73735115642-001	2.97373511561-002	1.11093077392-004	1.12292766154-003	-1.01383600114-003
	4.9304661684-001	2.99356666136-002	1.30871169257-004	1.16969875363-003	-1.03482704777-003
	5.1198287735-001	3.01319828771-002	1.64323132919-004	1.21646562574-003	-1.05314664322-003
	5.3029753757-001	3.03297537571-002	1.92853530374-004	1.26324069782-003	-1.0699554744-003
	5.4924191859-001	3.0526012967-002	2.3777193368-004	1.3101198988-003	-1.0722834374-003
	5.685785932-001	3.07239284582-002	2.8777193368-004	1.35678304196-003	-1.07103564312-003
	5.8782122011-001	3.09212639187-002	3.4273109246-004	1.40355411405-003	-1.06092301779-003
	6.0715306882-001	3.11185993792-002	4.1008440876-004	1.4503251616-003	-1.04823577916-003
	6.2645214072-001	3.13158748386-002	4.89577674406-004	1.49709625824-003	-1.00751857882-003
	6.45766081-001	3.15131982992-002	5.63177949442-004	1.54366733030-003	-9.60089330609-004
	6.6507640021-001	3.17105857597-002	6.33162571336-004	1.59064840235-003	-8.97475831024-004
	6.84382122011-001	3.19162122012-002	8.2131082392-004	1.63748947441-003	-8.15274392029-004
	7.03695214072-001	3.21051366403-002	9.73052150801-004	1.68418654652-003	-7.11128357728-004
	7.2300760801-001	3.23024521401-002	1.1493094469-003	1.73092161058-003	-5.81642124672-004
	7.4231760801-001	3.24997675017-002	1.35475242039-003	1.77772269080-003	-4.22970278234-004
	7.6162806121-001	3.26978038612-002	1.59432240184-003	1.82449376266-003	-2.30743260774-004
	7.809430852146-001	3.28943985217-002	1.87126953489-003	1.87126953489-003	1.78530255552-013

THERMAL STEADY STATE // PHOTOCHEMICAL STEADY STATE

J	1.70819016712-002	1.70819016712-002
T	1.9989560512-008	2.50817081674-002
A	3.06411028856-008	4.21951635244-007
L	5.93724489192-000	4.21951635244-007
DL	7.9364194953-000	5.90648172912-004
	9.86357489801-008	2.3703737039-005

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TIME	UT	DF	RA	GM	DC	DDI
0.000000000000	-7.25595510-005	-6.2504237-012	0.000000000000	-6.2504237-012	6.29045237-012	-9.55120091-005
1.000000000000	-7.25601021-005	-6.2505352-012	0.47347070-019	-6.2505352-012	6.28535139-012	-9.54980006-005
2.000000000000	-7.25606537-005	-6.2506463-012	1.000000000000	-6.2506463-012	6.28080740-012	-9.54758311-005
3.000000000000	-7.25612053-005	-6.2507574-012	1.52709911-010	-6.2507574-012	6.27612053-012	-9.54536616-005
4.000000000000	-7.25617569-005	-6.2508685-012	2.05420822-011	-6.2508685-012	6.27143369-012	-9.54314921-005
5.000000000000	-7.25623085-005	-6.2509796-012	2.58131733-011	-6.2509796-012	6.26674685-012	-9.54093226-005
6.000000000000	-7.25628601-005	-6.2510907-012	3.10842644-011	-6.2510907-012	6.26206001-012	-9.53871531-005
7.000000000000	-7.25634117-005	-6.2512018-012	3.63553555-011	-6.2512018-012	6.25737317-012	-9.53649836-005
8.000000000000	-7.25639633-005	-6.2513129-012	4.16264466-011	-6.2513129-012	6.25268633-012	-9.53428141-005
9.000000000000	-7.25645149-005	-6.2514240-012	4.68975377-011	-6.2514240-012	6.24800000-012	-9.53206446-005
10.000000000000	-7.25650665-005	-6.2515351-012	5.21686288-011	-6.2515351-012	6.24331316-012	-9.52984751-005
11.000000000000	-7.25656181-005	-6.2516462-012	5.74397200-011	-6.2516462-012	6.23862632-012	-9.52763056-005
12.000000000000	-7.25661697-005	-6.2517573-012	6.27108111-011	-6.2517573-012	6.23393948-012	-9.52541361-005
13.000000000000	-7.25667213-005	-6.2518684-012	6.79819022-011	-6.2518684-012	6.22925264-012	-9.52319666-005
14.000000000000	-7.25672729-005	-6.2519795-012	7.32530033-011	-6.2519795-012	6.22456580-012	-9.52097971-005
15.000000000000	-7.25678245-005	-6.2520906-012	7.85241044-011	-6.2520906-012	6.21987896-012	-9.51876276-005
16.000000000000	-7.25683761-005	-6.2522017-012	8.37952055-011	-6.2522017-012	6.21519212-012	-9.51654581-005
17.000000000000	-7.25689277-005	-6.2523128-012	8.90663066-011	-6.2523128-012	6.21050528-012	-9.51432886-005
18.000000000000	-7.25694793-005	-6.2524239-012	9.43374077-011	-6.2524239-012	6.20581844-012	-9.51211191-005
19.000000000000	-7.25700309-005	-6.2525350-012	9.96085088-011	-6.2525350-012	6.20113160-012	-9.50989496-005
20.000000000000	-7.25705825-005	-6.2526461-012	10.48796099-011	-6.2526461-012	6.19644476-012	-9.50767801-005
21.000000000000	-7.25711341-005	-6.2527572-012	11.01507110-011	-6.2527572-012	6.19175792-012	-9.50546106-005
22.000000000000	-7.25716857-005	-6.2528683-012	11.54218121-011	-6.2528683-012	6.18707108-012	-9.50324411-005
23.000000000000	-7.25722373-005	-6.2529794-012	12.06929132-011	-6.2529794-012	6.18238424-012	-9.50102716-005
24.000000000000	-7.25727889-005	-6.2530905-012	12.59640143-011	-6.2530905-012	6.17769740-012	-9.49881021-005
25.000000000000	-7.25733405-005	-6.2532016-012	13.12351154-011	-6.2532016-012	6.17301056-012	-9.49659326-005
26.000000000000	-7.25738921-005	-6.2533127-012	13.65062165-011	-6.2533127-012	6.16832372-012	-9.49437631-005
27.000000000000	-7.25744437-005	-6.2534238-012	14.17773176-011	-6.2534238-012	6.16363688-012	-9.49215936-005
28.000000000000	-7.25749953-005	-6.2535349-012	14.70484187-011	-6.2535349-012	6.15895004-012	-9.48994241-005
29.000000000000	-7.25755469-005	-6.2536460-012	15.23195198-011	-6.2536460-012	6.15426320-012	-9.48772546-005
30.000000000000	-7.25760985-005	-6.2537571-012	15.75906209-011	-6.2537571-012	6.14957636-012	-9.48550851-005
31.000000000000	-7.25766501-005	-6.2538682-012	16.28617220-011	-6.2538682-012	6.14488952-012	-9.48329156-005
32.000000000000	-7.25772017-005	-6.2539793-012	16.81328231-011	-6.2539793-012	6.14020268-012	-9.48107461-005
33.000000000000	-7.25777533-005	-6.2540904-012	17.34039242-011	-6.2540904-012	6.13551584-012	-9.47885766-005
34.000000000000	-7.25783049-005	-6.2542015-012	17.86750253-011	-6.2542015-012	6.13082900-012	-9.47664071-005
35.000000000000	-7.25788565-005	-6.2543126-012	18.39461264-011	-6.2543126-012	6.12614216-012	-9.47442376-005
36.000000000000	-7.25794081-005	-6.2544237-012	18.92172275-011	-6.2544237-012	6.12145532-012	-9.47220681-005
37.000000000000	-7.25799597-005	-6.2545348-012	19.44883286-011	-6.2545348-012	6.11676848-012	-9.46998986-005
38.000000000000	-7.25805113-005	-6.2546459-012	19.97594297-011	-6.2546459-012	6.11208164-012	-9.46777291-005
39.000000000000	-7.25810629-005	-6.2547570-012	20.50305308-011	-6.2547570-012	6.10739480-012	-9.46555596-005
40.000000000000	-7.25816145-005	-6.2548681-012	21.03016319-011	-6.2548681-012	6.10270796-012	-9.46333901-005
41.000000000000	-7.25821661-005	-6.2549792-012	21.55727330-011	-6.2549792-012	6.09802112-012	-9.46112206-005
42.000000000000	-7.25827177-005	-6.2550903-012	22.08438341-011	-6.2550903-012	6.09333428-012	-9.45890511-005
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13. ABSTRACT <p>The explosion limits associated with a given sample of an unstable compound are generally taken to be defined by the sample's temperature, pressure, composition, and size. In the presence of steady-state or pulsed radiative fields, these explosion limits are necessarily modified. Further photo-chemically significant radiation (e.g., U.V.) may play a markedly different role in this modification than does purely thermal radiation (I.R.). Examination is made of the role of both steady-state and pulsed radiative fields in the explosive behavior of unstable compounds. The analytic considerations are illustrated for the case of the mixed hydrazine family of reactants as well as for ozone.</p>			

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